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(54) Title: SUPPORTED GROUP 8-10 TRANSITION METAL OLEFIN POLYMERIZATION CATALYSTS

(57) Abstract

Methods for preparing olefin polymers, and catalysts for preparing olefin polymers are disclosed. The polymers can be prepared by contacting the corresponding monomers with a Group 8-10 transition metal catalyst and a solid support. The polymers are suitable for processing in conventional extrusion processes, and can be formed into high barrier sheets or films, or low molecular weight resins for use in synthetic waxes in wax coatings or as emulsions.

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Supported Group 8-10 Transition Metal Olefin Polymerization Catalysts

The present invention is directed to Group 8-10 transition metal-containing complexes, their use in olefin polymerizations, and to novel olefin polymers produced thereby.

Olefin polymers are used in a wide variety of products, from sheathing for wire and cable to film. Olefin polymers are used, for instance, in injection or compression molding applications, in extruded films or sheeting, as extrusion coatings on paper, for example photographic paper and digital recording paper, and the like. Improvements in catalysts have made it possible to better control polymerization processes, and, thus, influence the properties of the bulk material. Increasingly, efforts are being made to tune the physical properties of plastics for lightness, strength, resistance to corrosion, permeability, optical properties, and the like, for particular uses. Chain length, polymer branching and functionality have a significant impact on the physical properties of the polymer. Accordingly, novel catalysts are constantly being sought in attempts to obtain a catalytic process for polymerizing olefins which permits more efficient and better controlled polymerization of olefins.

Conventional polyolefins are prepared by a variety of polymerization techniques, including homogeneous liquid phase, gas phase, and slurry polymerization. Certain transition metal catalysts, such as those based on titanium compounds (e.g. $TiCl_3$ or $TiCl_4$) in combination with organoaluminum cocatalysts, are used to make linear and linear low density polyethylenes as well as poly-α-olefins such as polypropylene. These so-called "Ziegler-Natta" catalysts are quite sensitive to oxygen and are ineffective for the copolymerization of nonpolar and polar monomers.

Recent advances in non-Ziegler-Natta olefin polymerization catalysis include the following.

L. K. Johnson et al., WO Patent Application 96/23010, disclose the polymerization of olefins using cationic nickel, palladium, iron, and cobalt complexes containing diimine and bisoxazoline ligands. This document also describes the polymerization of ethylene, acyclic olefins, and/or selected cyclic olefins and optionally selected unsaturated acids or esters such as acrylic acid or alkyl acrylates to provide olefin homopolymers or copolymers.

European Patent Application Serial No. 381,495 describes the polymerization of olefins using palladium and nickel catalysts which contain selected bidentate phosphorous containing ligands.

L. K. Johnson et al., *J. Am. Chem. Soc.*, **1995**, *117*, 6414, describe the polymerization of olefins such as ethylene, propylene, and 1-hexene using cationic α-diimine-based nickel and palladium complexes. These catalysts have been described to polymerize ethylene to high molecular weight branched polyethylene. In addition to ethylene, Pd complexes act as catalysts for the polymerization and copolymerization of olefins and methyl acrylate.

G.F. Schmidt et al., *J. Am. Chem. Soc.* **1985**, *107*, 1443, describe a cobalt(III) cyclopentadienyl catalytic system having the structure $[C_5Me_5(L)CoCH_2CH_2\text{-}\mu\text{-}H]^+$, which provides for the "living" polymerization of ethylene.

M. Brookhart et al., *Macromolecules* **1995**, *28*, 5378, disclose using such "living" catalysts in the synthesis of end-functionalized polyethylene homopolymers.

U. Klabunde, U. S. Patents 4,906,754, 4,716,205, 5,030,606, and 5,175,326, describes the conversion of ethylene to polyethylene using anionic phosphorous, oxygen donors ligated to Ni(II). The polymerization reactions were run between 25 and 100°C with modest yields, producing linear polyethylene having a weight-average molecular weight ranging

between 8K and 350 K. In addition, Klabunde describes the preparation of copolymers of ethylene and functional group containing monomers.

M. Peuckert et al., *Organomet.* **1983**, *2*(5), 594, disclose the oligomerization of ethylene using phosphine, carboxylate donors ligated to Ni(II), which showed modest catalytic activity (0.14 to 1.83 TO/s). The oligomerizations were carried out at 60 to 95° C and 10 to 80 bar ethylene in toluene, to produce α-olefins.

R.E. Murray, U.S. Patents Nos. 4,689,437 and 4,716,138, describes the oligomerization of ethylene using phosphine, sulfonate donors ligated to Ni(II). These complexes show catalyst activities approximately 15 times greater than those reported with phosphine, carboxylate analogs.

W. Keim et al., *Angew. Chem. Int. Ed. Eng.* **1981**, *20*, 116, and V.M. Mohring, et al., *Angew. Chem. Int. Ed. Eng.* **1985**, *24*,1001, disclose the polymerization of ethylene and the oligomerization of α-olefins with aminobis(imino)phosphorane nickel catalysts; G. Wilke, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 185, describes a nickel allyl phosphine complex for the polymerization of ethylene.

K.A.O. Starzewski et al., *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 63, and U. S. Patent 4,691,036, describe a series of bis(ylide) nickel complexes, used to polymerize ethylene to provide high molecular weight linear polyethylene.

WO Patent Application 97/02298 discloses the polymerization of olefins using a variety of neutral N, O, P, or S donor ligands, in combination with a nickel(0) compound and an acid.

Brown et al., WO 97/17380, describes the use of Pd α-diimine catalysts for the polymerization of olefins including ethylene in the presence of air and moisture.

Fink et al., U. S. Patent No., 4,724,273, have described the polymerization of α-olefins using aminobis(imino)phosphorane nickel catalysts and the compositions of the resulting poly(α-olefins).

Recently Vaughan et al. WO 9748736, Denton et al. WO 9748742, and Sugimura et al. WO 9738024 have described the polymerization of ethylene using silica supported α-diimine nickel catalysts.

Additional recent developments are described by Sugimura et al., in JP96-84344, JP96-84343, by Yorisue et al., in JP96-70332, by Canich et al. WO 9748735, McLain et al. WO 9803559, Weinberg et al. WO 9803521 and by Matsunaga et al. WO 9748737.

Notwithstanding these advances in non-Ziegler-Natta catalysis, there remains a need for efficient and effective Group 8-10 transition metal catalysts for effecting polymerization of olefins. In addition, there is a need for novel methods of polymerizing olefins employing such effective Group 8-10 transition metal catalysts. In particular, there remains a need for Group 8-10 transition metal olefin polymerization catalysts with both improved temperature stability and functional group compatibility. Further, there remains a need for a method of polymerizing olefins utilizing effective Group 8-10 transition metal catalysts in combination with a Lewis acid so as to obtain a catalyst that is more active and more selective.

Brief Description of the Drawing

Figure 1 is a plot of weight fraction and cumulative weight fraction versus temperature in degree Celsius for four samples of polyethylene.

The following general procedure was used to generate this plot:

This data was collected using a Polymics™ CAP-TREF (Temperature Rising Elution Fractionation) system, by first preparing a one percent polymer solution in 1,2,4-trichlorobenzene. The samples were dissolved at 150 °C over two hours. An appropriate amount of CHROMASORB ™ P was added to the solution, placed in a temperature-

controlled oven and cooled at a rate of 2 °C per hour from 150 °C to 30 °C. The TREF analysis was performed by heating the material at 200 °C per hour at a solvent (1,2,4-trichlorobenzene) flow rate of 20 mL per minute.

The weight fraction was determined by percent transmittance of an infrared beam of light (3.41 μm).

Curve 1 is the weight fraction as a function of temperature of a polyethylene made in solution using the catalyst **XXVII**, at 80 °C and 600 psig (ethylene), as per Example 196. Average branching of 45 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Curve 2 is the weight fraction as a function of temperature of a polyethylene made in solution using the catalyst **XXVII**, at 80 °C and 600 psig (ethylene), as per Example 197. Average branching of 45 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Curve 3 is the weight fraction as a function of temperature of a polyethylene made in the gas phase using the silica-supported catalyst **XXVII**, at 100 °C and 100 psig (ethylene), as per Example 136. Average branching of 45 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Curve 4 is the weight fraction as a function of temperature of a polyethylene made in the gas phase using the silica-supported catalyst **XXVII**, at 100 °C and 100 psig (ethylene), as per Example 150. Average branching of 47 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Curve 1a is the cumulative weight fraction as a function of temperature for a polyethylene prepared in solution using the catalyst **XXVII**, at 80 °C and 600 psig (ethylene), as per Example 196. Average branching of 45 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Curve 2a is the cumulative weight fraction as a function of temperature for a polyethylene prepared in solution using the catalyst

XXVII, at 80 °C and 600 psig (ethylene), as per Example 197. Average branching of 45 branches/1000 carbon atoms, as determined by ^{1}H NMR.

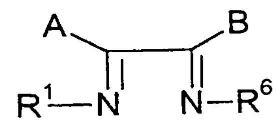
Curve 3a is the cumulative weight fraction as a function of temperature for a polyethylene prepared in gas phase using the silica-supported catalyst **XXVII**, at 100 °C and 100 psig (ethylene), as per Example 136. Average branching of 45 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Curve 4a is the cumulative weight fraction as a function of temperature for a polyethylene prepared in gas phase using the silica-supported catalyst **XXVII**, at 100 °C and 100 psig (ethylene), as per Example 150. Average branching of 47 branches/1000 carbon atoms, as determined by ^{1}H NMR.

Figure 1 illustrates the unique compositions prepared in the gas phase using supported catalysts of the present invention. The polymers prepared using a homogeneous catalyst in solution (i.e., 1 and 2) dissolve over a relatively narrow temperature range, while those prepared using a supported catalyst in the gas phase (i.e., 3 and 4) dissolve over a much wider temperature range. Thus, the comparison of curves 1 and 2 versus curves 3 and 4 indicates the existence of a narrow composition distribution range for the polyethylenes made in solution, in sharp contrast to the polyethylenes prepared using gas phase polymerization while using the same transition metal complex when attached to a solid support. As can be seen in Figure 1, curves 3 and 4 depict dissolution over a much larger temperature range, evidence of a much broader composition distribution.

In this regard, such polymer compositions provide a unique blend of properties, i.e., a balance of impact, toughness, elasticity, tear-resistance, and puncture resistance, which are particularly desired for such end uses as film, packaging, sheeting, etc.

In one embodiment, the present invention provides a catalyst for the polymerization of olefins comprising a complex comprising (a) a ligand of the formula **X**, (b) a group 8-10 transition metal, and optionally (c) a Bronsted or Lewis acid,



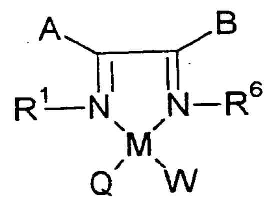
X

R^1 and R^6 are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the Bronsted or Lewis acid, and the complex are combined in any order to form said catalyst.

In the above catalyst, it should be appreciated that the Group 8-10 transition metal has coordinated thereto a bidentate ligand having the formula **X** and that the Bronsted or Lewis acid is optionally reacted with this metal-ligand complex. In addition, the Bronsted or Lewis acid may be optionally combined with the ligand **X** prior to complexation to the Group 8-10 transition metal.

In one embodiment, the invention provides a catalyst for the polymerization of olefins comprising the reaction product of a compound of formula **XII**, a compound Y and a solid support:



XII

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

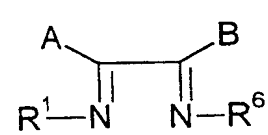
W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

As a further aspect of the invention, there is provided a process for the preparation of supported catalysts comprising contacting a group 8-10 transition metal complex of a ligand of the formula **X**, a solid support, and optionally a Bronsted or Lewis acid,

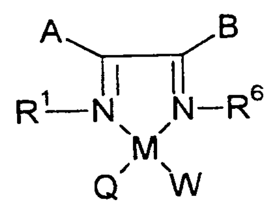


X

wherein R^1 and R^6 are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the Bronsted or Lewis acid, and the complex are combined in any order to form said supported catalyst.

In a further embodiment, there is provided a process for the preparation of supported catalysts comprising the reaction product of a compound of formula **XII**, a compound Y and a solid support:



XII

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

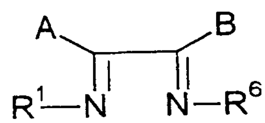
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a

cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

In a further embodiment, there is provided a process for the polymerization of olefins, comprising contacting one or more monomers of the formula $RCH{=}CHR^8$ with a catalyst comprising a group 8-10 transition metal complex of a ligand of the formula **X** and optionally a Bronsted or Lewis acid,



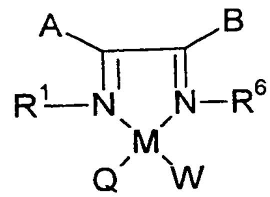
X

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R^1 and R^6 are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; **N** represents nitrogen; and

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the Bronsted or Lewis acid, and the complex are combined in any order.

In a further embodiment, the present invention provides a process for the polymerization of olefins, comprising contacting one or more monomers of the formula $RCH{=}CHR^8$ with the reaction product of a compound of formula **XII**, a compound Y and a solid support:



XII

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

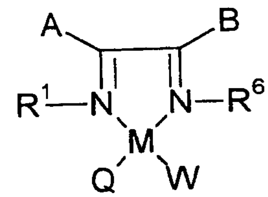
W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

In a further embodiment, the present invention provides a process for the polymerization of olefins, comprising contacting one or more monomers of the formula $RCH{=}CHR^8$ with a supported catalyst formed by combining a compound of formula **XII**:



XII

with a solid support which has been pre-treated with a compound Y,

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

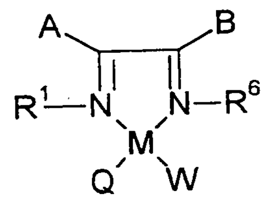
and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

In a further embodiment, a process for the copolymerization of one or more olefin monomers of the type $RCH{=}CHR^8$ with one or more functional olefin monomers of the formula $CH_2{=}CH(CH_2)_nJ$ comprising a catalyst, in an olefin polymerization reaction which comprises combining a complex of the formula **XII**, a solid support, and optionally a compound Y, prior to the utilization of said catalyst in said olefin polymerization reaction.

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

n is an interger between 1-20;

J is a group selected from ester, acyl, acid halide, aldehyde, alkyl amide, aryl, alkylamine, aryl amine, alkyl amido, aryl amido, alkyl imido, aryl imido, ether, nitrile, alcohol, keto, amino, amido, imido, alkoxy thiol, thioalkoxy, acid, urea, sulfonamido, and sulfoester;



XII

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

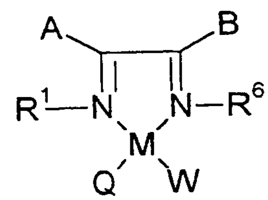
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

In a further preferred embodiment, the present invention provides a process for the copolymerization of ethylene and a comonomer of the formula $CH_2{=}CH(CH_2)_nCO_2R^1$ which comprises contacting ethylene and a comonomer of the formula $CH_2{=}CH(CH_2)_nCO_2R^1$ with a supported catalyst

formed by combining silica with a compound of the formula **XII** and optionally a compound Y;



XII

wherein R^1 is hydrogen, hydrocarbyl, substituted hydrocarbyl, fluoroalkyl or silyl;

n is an integer greater than 3;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

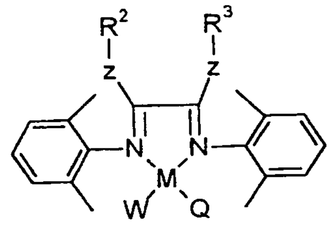
W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

In a further preferred embodiment, there is provided the above process wherein the compound of formula **XII** is represented by formula **XXIV**.



XXIV

wherein R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl, or may collectively form a bridging hydrocarbyl, bridging substituted hydrocarbyl, or a substituted silicon atom;

Q is alkyl, chloride, iodide or bromide;

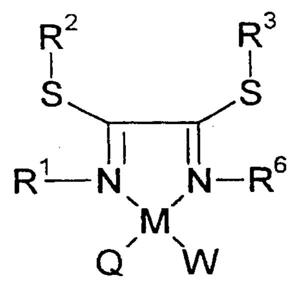
W is alkyl, chloride, iodide or bromide;

N is nitrogen;

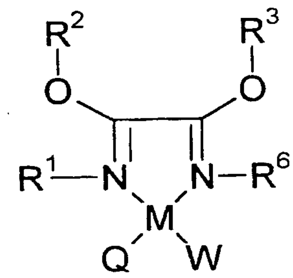
Z is sulfur or oxygen; and

M is Ni(II).

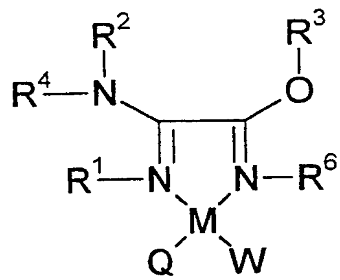
In a further preferred embodiment, there is provided a supported catalyst comprising the reaction product of a compound of formula **V**, **VIII**, or **XV**:



V



VIII



XV

wherein R^1 and R^6 each, independently, represent a sterically hindered aryl;

R^2, R^3 and R^4 each, independently, represent a hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl, and, in addition, may collectively form a bridging hydrocarbyl, bridging substituted hydrocarbyl, or a substituted silicon atom;

Q represents a hydrocarbyl, chloride, iodide or bromide;

W represents a hydrocarbyl, chloride, iodide or bromide;

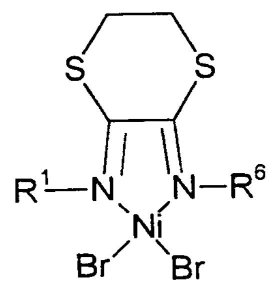
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

with a solid support which has been pre-treated with a compound Y, wherein Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a

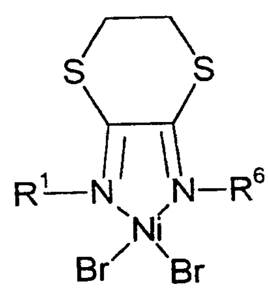
cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

In an especially preferred embodiment, the compound of formula **XII** is selected from the group consisting of



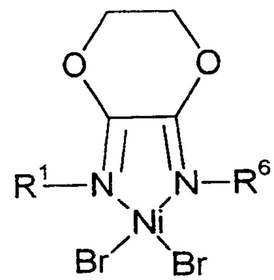
XXVII

wherein R^1 and R^6 are 2,6-dimethylphenyl;



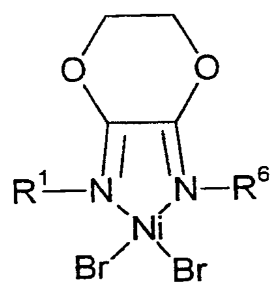
XXVIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;



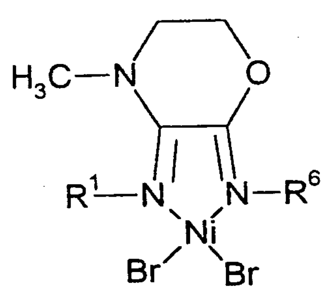
XXXII

wherein R^1 and R^6 are 2,6-dimethylphenyl;



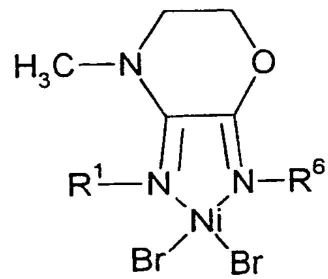
XXXIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;



XXXVIII

wherein R^1 and R^6 are 2,6-dimethylphenyl; and



XXXIX

wherein R^1 and R^6 are 2,6-diisopropylphenyl.

The catalysts used in the processes of the present invention readily convert ethylene and α-olefins to high molecular weight polymers, and allow for olefin polymerizations under various conditions, including ambient temperature and pressure, including gas phase and slurry (e.g., slurry loop).

As noted herein, it is preferred that the compounds of the present invention be attached to a solid support which has been pre-treated with a compound Y, for example, MAO, or mixed with Y in any order. We have discovered that when such supported catalysts are used in slurry and gas phase ethylene polymerizations, novel polymer compositions are provided insofar as such compositions are blends of different polyolefin polymers. It is believed that when such catalysts are attached to a solid support, such as silica, olefin polymerizations using such supported catalysts provide a polymer composition which possesses a broad compositional distribution. This is believed to be due at least in part to both the creation of unique reaction sites, and the sensitivity of these catalysts to ethylene concentration. These unique reaction sites are believed to result from the unique microenvironments created by the location of the catalyst on the support. The resulting polymer composition, which can be prepared solely from ethylene as an olefin feedstock, is one which is actually a blend or plurality of polymers having a variety of alkyl branched distributions with

some catalyst sites giving less branched high density polymer and other sites giving more branched lower density polymer.

The present invention also provides novel polyalkene compositions. Thus, in one embodiment, the present invention provides polyethylene composition comprising a blend of polyethylene polymers, wherein said blend has an average degree of branching of from 5 to 120 alkyl branches per 1000 carbon atoms, wherein any individual component of said blend has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms, wherein said polymers are prepared in one reaction vessel, solely from ethylene, and wherein said polymers are prepared utilizing a Group 8-10 transition metal catalyst supported on a solid support which has been pre-treated with a compound Y selected from the group consisting of methylaluminoxane and other aluminum sesquioxides having the formulas $R^7{}_3Al$, $R^7{}_2AlCl$, and R^7AlCl_2 ,wherein R^7 is alkyl. The transition metal is preferably Ni and the compound Y is methylaluminoxane

A further embodiment of the invention provides a polyethylene composition comprising a blend of polyethylene polymers, wherein said blend has an average degree of branching from 5 to 120 alkyl branches per 1000 carbon atoms, wherein any individual component of said blend has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms, wherein said polymers are prepared in one reaction vessel, solely from ethylene, and wherein said polymers are prepared utilizing a Group 8-10 transition metal catalyst which has been reacted with a solid support and a compound Y, in any order, wherein Y is selected from the group consisting of methylaluminoxane and other aluminum sesquioxides having the formulas $R^7{}_3Al$, $R^7{}_2AlCl$, and R^7AlCl_2 ,wherein R^7 is alkyl.

Further, the catalysts of this invention when supported in this fashion and utilized in a gas or slurry phase process provide polymers having a broad composition distribution while having an intermediate molecular weight distribution, thus providing certain processing advantages. When

fractionated based on solubility using supercritical propane by isothermal increasing profiling and critical, isobaric, temperature rising elution fractionation, into ten fractions, an analysis of such fractions provides data on the distribution of the relative branching of the components of said composition.

Thus, in a further embodiment, there is provided a polyolefin which when fractionated based on solubility using supercritical propane by isothermal increasing profiling and critical, isobaric, temperature rising elution fractionation, into ten fractions between about 40 and about 140 °C, wherein a first fraction taken at about 40 °C has between about 40 and about 100 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 and about 15% are pentyl or longer branches; a second fraction taken between about 40-60 °C has between about 30 and about 90 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 and about 15% are pentyl or longer branches; a third fraction taken between about 60-65 °C has between about 30 and about 80 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 to about 15% are pentyl or longer branches; a fourth fraction taken between about 65-70 °C has between about 20 and about 60 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 to about 15% are pentyl or longer branches; a fifth fraction taken between about 75-

85 °C has between about 10 and about 50 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 to about 15% are pentyl or longer branches; a sixth fraction taken between about 85-95 °C has between about 10 and about 40 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 and about 15% are pentyl or longer branches; a seventh fraction taken between about 95-100 °C has between about 5 and about 35 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 and about 15% are pentyl or longer branches; an eighth fraction taken between about 100-110 °C has between about 0 and about 25 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 and about 15% are pentyl or longer branches; a ninth fraction taken between about 110-140 °C has between about 0 and about 30 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 to about 15% are pentyl or longer branches; a tenth fraction taken between about 140-150 °C has between about 0 and about 20 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 to about 15% are pentyl or longer

branches, and a tenth fraction has between about 0 and about 20 branches per 1000 carbon atoms.

In contrast to a polymer prepared by solution polymerization, where the melting temperature as defined by the endothermic maximum is inversely correlated with the average degree of branching of said polymer, the polymers prepared from the supported catalysts of the present invention exhibit a relatively constant melting temperature (endothermic maximum) over a relatively wide range of average branching. In certain cases, this also provides a free flowing powder which is again, a significant processing advantage in the gas phase.

In a further embodiment, there is provided a polymer derived from essentially ethylene alone that has greater than 30 branches per 1000 carbon atoms and a melt transition (endothermic maximum) in the DSC of greater than about 110 °C. Preferably, the polymer is a free flowing polymer.

In a further embodiment, there is provided a polymer derived from ethylene alone that has a broad composition distribution and a molecular weight distribution of less than 6 and greater than 2.5, wherein said polymer has an average degree of branching of from 5 to 120 alkyl branches per 1000 carbon atoms, and wherein any individual component of said polymer has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms. In such polymer compositions, it is preferred that an individual component of the polymer has between about 40 and 100 branches per 1000 carbon atoms, another component has between about 30 and 90 branches per 1000 carbon atoms, another component has between about 30 and 80 branches per 1000 carbon atoms, another component has between about 20 and 60 branches per 1000 carbon atoms, another component has between about 10 and 50 branches per 1000 carbon atoms, another component has between about 10 and 40 branches per 1000 carbon atoms, another component has between about 5 and 35

branches per 1000 carbon atoms, another component has between about 0 and 25 branches per 1000 carbon atoms, another component has between about 0 and 30 branches per 1000 carbon atoms, another component has between about 0 and 20 branches per 1000 carbon atoms.

We have also recognized that by attaching a Group 8-10 polymerization catalyst to a solid support one can improve its functional group compatibility over that observed in the homogenous solution polymerization. In other words, the rate for the co-polymerization of one or more olefin monomers of the type $RCH{=}CHR^8$ with one or more functional olefin monomers of type $CH_2{=}CH(CH_2)_nJ$ is increased over the homogeneous solution polymerization run under otherwise identical conditions. In particular, we have found that by utilizing a supported Group 8-10 catalyst that monomers of the general formula $CH_2{=}CH(CH_2)_nJ$ are copolymerized with other olefins (e.g. ethylene) at rates several orders of magnitude greater than that observed for corresponding homogeneous systems. In this regard, examples of Group 8-10 catalysts useful in this process include those described in US Patent Numbers 5,866,663; 5,886,224; 5,891,963; 5,880,323; 5,880,241 are incorporated herein by reference, along with WO9623010, WO9910391, WO 9905189, WO 9856832, WO 9803559, WO 9847934, WO9702298, WO 9830609, WO 9842665, WO 9842664, WO 9847933, WO 9840420, WO 9840374.

Thus, in a further embodiment, there is provided a Group 8-10 transition metal catalyst having an improved rate for the co-polymerization of one or more olefin monomers of the type $RCH{=}CHR^8$ with one or more functional olefin monomers of the formula $CH_2{=}CH(CH_2)_nJ$, in an olefin polymerization reaction which comprises combining said catalyst with a solid support, and optionally a Bronsted or Lewis acid in any order, prior to the utilization of said catalyst in said olefin polymerization reaction.

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

n is an interger between 1-20;

J is a group selected from ester, acyl, acid halide, aldehyde, alkyl amide, aryl, alkylamine, aryl amine, alkyl amido, aryl amido, alkyl imido, aryl imido, ether, nitrile, alcohol, keto, amino, amido, imido, alkoxy thiol, thioalkoxy, acid, urea, sulfonamido, and sulfoester. Preferably, the compound of the formula $CH_2=CH(CH_2)_nJ$ is a compound of the formula $CH_2=CH(CH_2)_nCO_2R^1$, wherein R^1 is hydrogen, hydrocarbyl, substituted hydrocarbyl, fluoroalkyl or silyl; and

n is an integer greater than 3;

In a further embodiment, the present invention provides an ethylene homopolymer with a CDBI of less than 50 %, preferably less than 40%, and more preferably less than 30%.

In a further embodiment, the present invention provides a polyalkene with a CDBI of less than 50%, which contains about 80 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches. Further preferred is a polyalkene of with a CDBI of less than 40%, more preferably less than 30%. Further preferred are those polyalkenes which contain about 100 to about 130 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 50 to about 75 ethyl branches, about 5 to about 15 propyl branches, about 24 to about 40 butyl branches, about 5 to about 10 amyl branches, and about 65 to about 120 hexyl or longer branches.

In a further embodiment, there is provided a polyalkene with a CDBI of less than 50% which contains about 20 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, 1 to about 12 propyl branches, 1 to about 12 butyl branches, 1 to about 10 amyl branches, and 0 to about

20 hexyl or longer branches. Further preferred are the polyalkenes with a CDBI of less than 40%, more preferably less than 30%. Further preferred embodiments include the polyalkenes which contains about 40 to about 100 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 6 to about 15 ethyl branches, about 2 to about 10 propyl branches, about 2 to about 10 butyl branches, about 2 to about 8 amyl branches, and about 2 to about 15 hexyl or longer branches.

The polymers of the present invention include homopolymers of olefins, such as polyethylene, polypropylene, and the like, and olefin copolymers, including functional-group containing copolymers. As an example, ethylene homopolymers can be prepared with strictly linear to highly branched structures by variation of the catalyst structure, cocatalyst composition, and reaction conditions, including pressure and temperature. The effect these parameters have on polymer structure is described herein. These polymers and copolymers have a wide variety of applications, including use as packaging material and in adhesives.

In this disclosure certain chemical groups or compounds are described by certain terms and symbols. These terms are defined as follows:

Symbols ordinarily used to denote elements in the Periodic Table take their ordinary meaning, unless otherwise specified. Thus, N, O, S, P, and Si stand for nitrogen, oxygen, sulfur, phosphorus, and silicon, respectively.

Examples of neutral Lewis acids include, but are not limited to, methylaluminoxane (hereinafter MAO) and other aluminum sesquioxides, $R^7{}_3Al$, $R^7{}_2AlCl$, R^7AlCl_2 (where R^7 is alkyl), organoboron compounds, boron halides, $B(C_6F_5)_3$, BPh_3, and $B(3,5\text{-}(CF_3)_2C_6H_3)_3$. Examples of ionic compounds comprising a cationic Lewis acid include: $R^9{}_3Sn[BF_4]$, (where R^9 is hydrocarbyl), $MgCl_2$, and H^+X^-, where X^- is a weakly coordinating anion.

The term "weakly coordinating anion" is well-known in the art *per se* and generally refers to a large bulky anion capable of delocalization of the negative charge of the anion. Suitable weakly coordinating anions include, but are not limited to, PF_6^-, BF_4^-, SbF_6^-, $(Ph)_4B^-$ wherein Ph = phenyl, $^-BAr_4$ wherein $^-BAr_4$ = tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. The coordinating ability of such anions is known and described in the literature (Strauss, S. et al., *Chem. Rev.* **1993**, *93*, 927).

Examples of neutral Lewis bases include, but are not limited to, (i) ethers, for example, diethyl ether or tetrahydrofuran, (ii) organic nitriles, for example acetonitrile, (iii) organic sulfides, for example dimethylsulfide, or (iv) monoolefins, for example, ethylene, hexene or cyclopentene.

A "hydrocarbyl" group means a monovalent or divalent, linear, branched or cyclic group which contains only carbon and hydrogen atoms. Examples of monovalent hydrocarbyls include the following: C_1-C_{20} alkyl; C_1-C_{20} alkyl substituted with one or more groups selected from C_1-C_{20} alkyl, C_3-C_8 cycloalkyl or aryl; C_3-C_8 cycloalkyl; C_3-C_8 cycloalkyl substituted with one or more groups selected from C_1-C_{20} alkyl, C_3-C_8 cycloalkyl or aryl; C_6-C_{14} aryl; and C_6-C_{14} aryl substituted with one or more groups selected from C_1-C_{20} alkyl, C_3-C_8 cycloalkyl or aryl; where the term "aryl" preferably denotes a phenyl, napthyl, or anthracenyl group. Examples of divalent (bridging) hydrocarbyls include: $-CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, and 1,2-phenylene.

A "silyl" group refers to a SiR_3 group wherein Si is silicon and R is hydrocarbyl or substituted hydrocarbyl or silyl, as in $Si(SiR_3)_3$.

A "heteroatom" refers to an atom other than carbon or hydrogen. Preferred heteroatoms include oxygen, nitrogen, phosphorus, sulfur, selenium, arsenic, chlorine, bromine, silicon and fluorine.

A "substituted hydrocarbyl" refers to a monovalent or divalent hydrocarbyl substituted with one or more heteroatoms. Examples of monovalent substituted hydrocarbyls include: 2,6-dimethyl-4-

methoxyphenyl, 2,6-diisopropyl-4-methoxyphenyl, 4-cyano-2,6-dimethylphenyl, 2,6-dimethyl-4-nitrophenyl, 2,6-difluorophenyl, 2,6-dibromophenyl, 2,6-dichlorophenyl, 4-methoxycarbonyl-2,6-dimethylphenyl, 2-tert-butyl-6-chlorophenyl, 2,6-dimethyl-4-phenylsulfonylphenyl, 2,6-dimethyl-4-trifluoromethylphenyl, 2,6-dimethyl-4-trimethylammoniumphenyl (associated with a weakly coordinated anion), 2,6-dimethyl-4-hydroxyphenyl, 9-hydroxyanthr-10-yl, 2-chloronapth-1-yl, 4-methoxyphenyl, 4-nitrophenyl, 9-nitroanthr-10-yl, $-CH_2OCH_3$, cyano, trifluoromethyl, or fluoroalkyl. Examples of divalent (bridging) substituted hydrocarbyls include: 4-methoxy-1,2-phenylene, 1-methoxymethyl-1,2-ethanediyl, 1,2-bis(benzyloxymethyl)-1,2-ethanediyl, or 1-(4-methoxyphenyl)-1,2-ethanediyl.

A "sterically hindered aryl" means (i) a phenyl ring with hydrocarbyl, substituted hydrocarbyl, F, Cl, Br or silyl substituents at both the 2- and 6-positions, optionally substituted elsewhere with hydrocarbyl, substituted hydrocarbyl, F, Cl, Br, silyl, hydroxy, methoxy, nitro, cyano, phenylsulfonyl, CO_2Me, CO_2H, $C(O)CH_3$, CF_3, or fluoroalkyl substituents, (ii) a 2-substituted napth-1-yl ring, optionally substituted elsewhere with hydrocarbyl, substituted hydrocarbyl, F, Cl, Br, silyl, hydroxy, methoxy, nitro, cyano, phenylsulfonyl, CO_2Me, CO_2H, $C(O)CH_3$, CF_3, or fluoroalkyl substituents, (iii) an 9-anthracenyl or 1,2,3,4,5,6,7,8-octahydro-9-anthracenyl ring, optionally substituted elsewhere with hydrocarbyl, substituted hydrocarbyl, F, Cl, Br, silyl, hydroxy, methoxy, nitro, cyano, phenylsulfonyl, CO_2Me, CO_2H, $C(O)CH_3$, CF_3, or fluoroalkyl substituents, or (iv) an aromatic substituted hydrocarbyl with steric properties functionally equivalent (in the context of this invention) to one or more of the following sterically hindered aryls: 2,6-dimethylphenyl, 2,4,6-trimethylphenyl, 2,6-diisopropylphenyl, 2,6-dimethyl-4-nitrophenyl, 2,6-dimethyl-4-phenylsulfonylphenyl, 2-isopropyl-6-methylphenyl, 2,6-bis(trifluoromethyl)phenyl, 2,6-dimethyl-4-methoxyphenyl, 2-methylnapth-1-yl, 9-anthracenyl, 1,2,3,4,5,6,7,8-octahydro-9-anthracenyl,

2,6-diclorophenyl, 2,6-dibromophenyl, 2-tert-butyl-6-methylphenyl, 2-trimethylsilylnapth-1-yl, 2-chloro-6-methylphenyl, 4-cyano-2,6-dimethylphenyl, 2,6-diisopropyl-4-methoxyphenyl, 2,4,6-tri-tert-butylphenyl, and 2-chloro-6-tert-butylphenyl.

A "heteroatom connected mono-radical" refers to a mono-radical group in which a heteroatom serves as the point of attachment. Examples include: NH(2,6-dimethylphenyl) and SPh, where Ph is phenyl. Numerous other examples are given herein.

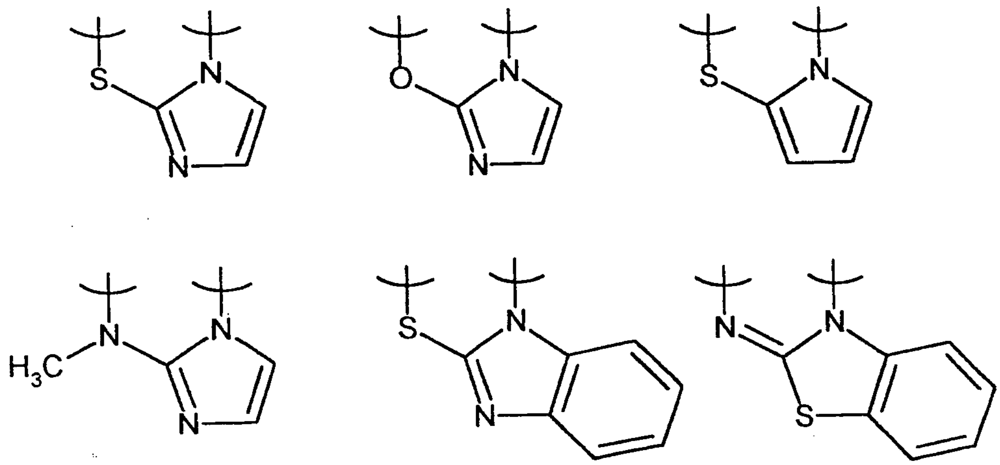
A "substituted silicon atom" refers to a $-SiR^9{}_2-$ group, wherein R^9 is a hydrocarbyl or substituted hydrocarbyl.

A "substituted phosphorous atom" refers to a $-P(O)(OR^9)-$ group, wherein R^9 is a hydrocarbyl or substituted hydrocarbyl.

A "substituted sulfur atom" refers to a -S(O)-, $-SO_2-$, or $-S(NR^9)_2-$ group, wherein R^9 is a hydrocarbyl or substituted hydrocarbyl.

A "bridging group" refers to a divalent hydrocarbyl, divalent substituted hydrocarbyl, -C(O)-, -C(S)-, substituted silicon atom, substituted sulfur atom, substituted phosphorous atom, $-CH_2C(O)-$, -C(O)C(O)-, or 3,4,5,6-tetrafluoro-1,2-phenylene.

In certain cases, the bridging group, together with groups **A** and **B**, may collectively form a divalent heteroatom-substituted heterocycle; examples include:



A "mono-olefin" refers to a hydrocarbon containing one carbon-carbon double bond.

A "suitable metal precursor" refers to a Group 8-10 transition metal compound, preferably Ni, Co, Pd, and Fe compounds, which may be combined with compound **X** (preferably, compound **III**, **VI**, **IX**, **XVII** or **XVIII**, described below), and optionally a Lewis or Bronsted acid, to form an active olefin polymerization catalyst. Examples include: (1,2-dimethoxyethane)nickel(II) dibromide, bis[(μ-chloro)(1, 2, 3-η^3-2-propenyl)nickel(II)], bis[(μ-chloro)(1, 2, 3-η^3-2-propenyl)palladium(II)], bis[(μ-chloro)(1, 2, 3-η^3-1-trimethylsilyloxy-2-propenyl)nickel(II)], $CoBr_2$, $FeBr_2$, bis(acetylacetonate)Ni(II), and [tetrakis(acetonitrile)Pd(II)][BF_4].

A "suitable nickel precursor" refers to a suitable metal precursor wherein the metal is nickel.

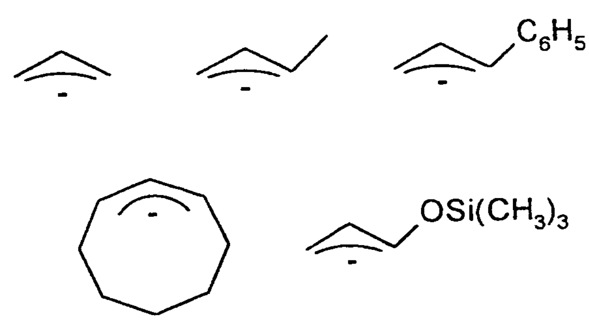
A "suitable nickel(0) precursor" refers to a suitable metal precursor which is a zerovalent nickel compound.

The term "fluoroalkyl" as used herein refers to a C_1-C_{20} alkyl group substituted by one or more fluorine atoms.

The term "polymer" as used herein is meant a species comprised of monomer units and having a degree of polymerization (DP) of ten or higher.

The term "α-olefin" as used herein is a 1-alkene with from 3 to 40 carbon atoms.

A "π-allyl" group refers to a monoanionic group with three sp^2 carbon atoms bound to a metal center in a η^3-fashion. Any of the three sp^2 carbon atoms may be substituted with a hydrocarbyl, substituted hydrocarbyl, heteroatom connected hydrocarbyl, heteroatom connected substituted hydrocarbyl, or O-silyl group. Examples of π-allyl groups include:



The term π-benzyl group denotes an π-allyl group where two of the sp^2 carbon atoms are part of an aromatic ring. Examples of π-benzyl groups include:

A polymer with a "broad composition distribution" refers to a polymer that comprises a plurality of compositions (preferably >5) having varying levels of branching. The polymers can be fractionated and the fractions have levels of branching/1000 carbons that range from about 0 to about 100 branches/1000 carbons.

"Composition Distribution Breadth Index" or CDBI is defined as the weight percent of the polymer molecules having a branching content within 50% (that is, 25% on each side of the average total branching) of the average total branching of the bulk sample as determined by ^1H NMR. The CDBI is readily determined using well known fractionation techniques such as temperature rising elution fractionation (TREF). (See also WO 97/48735 and WO 93/03093).

Sample calculation:

-bulk polymer has 40 branches/1000 carbon atoms

-30———40———50 (degree of branching within 50% of the average branching for bulk sample)

-fractionate polymer using TREF or other technique

-calculate the weight percent of the total polymer that has total branches as determined by NMR between 30 and 50. e.g. 5 grams of the total 10 grams charged when fractionated and analyzed has branching between 30 and 50 branches/1000 carbon atoms. CDBI for this polymer would be 50%.

A "free flowing polymer" refers to a non-tacky polymer that can be transported without significant agglomeration. In this context, this lack of significant agglomeration refers to polymer products which are useful under commercial gas phase reactor conditions.

As used herein, the terms "monomer" and "olefin monomer" refer to the olefin or other monomer compound before it has been polymerized; the term "monomer units" refers to the moieties of a polymer that correspond to the monomers after they have been polymerized.

In some cases, a compound Y is required as a cocatalyst. Suitable compounds Y include a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, or a Bronsted acid whose conjugate base is a weakly coordinating anion. Preferred compounds Y include: methylaluminoxane (hereinafter MAO) and other aluminum sesquioxides, $R^7{}_3Al$, $R^7{}_2AlCl$, R^7AlCl_2 (wherein R^7 is alkyl), organoboron compounds, boron halides, $B(C_6F_5)_3$, $R^9{}_3Sn[BF_4]$ (wherein R^9 hydrocarbyl), $MgCl_2$, and H^+X^-, wherein X^- is a weakly coordinating anion. Examples of H^+X^- are the

ether solvate of hydrogen tetrakis[3,5-bis(trifluoromethyl)phenyl]borate and montmorillinite clay.

Examples of "solid support" include inorganic oxide support materials, such as: talcs, silicas, titania, silica/chromia, silica/chromia/titania, silica/alumina, zirconia, aluminum phosphate gels, silanized silica, silica hydrogels, silica xerogels, silica aerogels, montmorillonite clay and silica co-gels as well as organic solid supports such as polystyrene and functionalized polystyrene. (See, for example, Roscoe, S.B.; Frechet, J.M.J.; Walzer, J.F.; Dias, A.J.; "Polyolefin Spheres from Metallocenes Supported on Non-Interacting Polystyrene", 1998, Science, 280, 270-273 (1998).) An especially preferred solid support is one which has been pre-treated with Y compounds as described herein, most preferably with MAO. Thus, in a preferred embodiment, the catalysts of the present invention are attached to a solid support (by "attached to a solid support" is meant ion paired with a component on the surface, adsorbed to the surface or covalently attached to the surface) which has been pre-treated with a compound Y. Alternatively, the catalyst, the compound Y, and the solid support can be combined in any order, and any number of Y compounds can be utilized; in addition, the supported catalyst thus formed, may be treated with additional quantities of compound(s) Y. In an especially preferred embodiment, the compounds of the present invention are attached to silica which has been pre-treated with MAO. Such supported catalysts are prepared by contacting the transition metal compound, in a substantially inert solvent--by which is meant a solvent which is either unreactive under the conditions of catalyst preparation, or if reactive, acts to usefully modify the catalyst activity or selectivity--with MAO treated silica for a sufficient period of time to generate the supported catalysts. Examples of substantially inert solvents include toluene, mineral spirits, hexane, CH_2Cl_2 and $CHCl_3$.

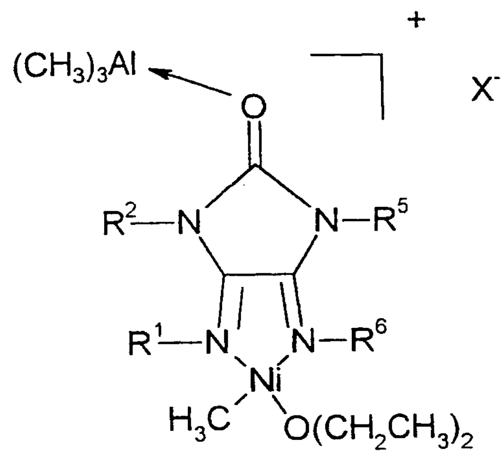
It is known to those skilled in the art that a variety of protocols may be used to generate active polymerization catalysts comprising transition metal complexes of various nitrogen, phosphorous, oxygen and sulfur donor ligands. Examples of such protocols include (i) the reaction of a Group 8-10 metal dihalide complex of a bidentate N-donor ligand with an alkylaluminum reagent, (ii) the reaction of a bidentate N-donor ligand with nickel(1,5-cyclooctadiene)$_2$ and HB(3,5-bis(trifluoromethyl)phenyl)$_4$, and (iii) the reaction of a Group 8-10 metal dialkyl complex of a bidentate N-donor ligand with MAO or HB(3,5-bis(trifluoromethyl)phenyl)$_4$. In some cases, it is also possible to react a bidentate N-donor ligand with nickel(1,5-cyclooctadiene)$_2$ and $B(C_6F_5)_3$ to obtain an active catalyst. Cationic (ligand)M(π-allyl) complexes with weakly coordinating counteranions, where M is a Group 8-10 transition metal, are often suitable as catalyst precursors, requiring only exposure to olefin monomer and in some cases elevated temperatures (40-200°C) or added Lewis acid, or both, to form an active polymerization catalyst.

Isolable [(ligand)Ni(methyl)(O(CH$_2$CH$_3$)$_2$)][B(3,5-bis(trifluoromethyl)phenyl)$_4$] and [(ligand)Pd(methyl)(O(CH$_2$CH$_3$)$_2$)][B(3,5-bis(trifluoromethyl)phenyl)$_4$] salts may also serve as one component catalyst systems. More generally, a variety of (ligand)M(Q)(W) complexes, where "ligand" refers to a compound of formula **X**, M is a divalent Group 8-10 transition metal, and Q and W are univalent groups, or may be taken together to form a divalent group, may be reacted with one or more compounds, collectively referred to as compound Y, which function as co-catalysts or activators, to generate an active catalyst of the form $[(\text{ligand})M(T)(L)]^+X^-$, where T is a hydrogen atom or hydrocarbyl, L is an olefin or neutral donor group capable of being displaced by an olefin, and X^- is a weakly coordinating anion.

When Q and W are both halide, examples of suitable compounds Y include: methylaluminoxane (hereinafter "MAO") and other aluminum

sesquioxides, $R^0{}_3Al$, $R^0{}_2AlCl$, and R^0AlCl_2 (wherein R^0 is alkyl). When Q and W are both alkyl, examples of suitable compounds Y include: MAO and other aluminum sesquioxides, $R^0{}_3Al$, $R^0{}_2AlCl$, R^0AlCl_2 (wherein R^0 is alkyl), $B(C_6F_5)_3$, $R^{16}{}_3Sn[BF_4]$, H^+X^-, wherein X^- is a weakly coordinating anion, for example, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, and Lewis acidic or Bronsted acidic metal oxides, for example, montmorillonite clay. In some cases, for example, when Q and W are both halide or carboxylate, sequential treatment with a metal hydrocarbyl, followed by reaction with a Lewis acid or Bronsted acid, may be required to generate an active catalyst. Suitable examples of metal hydrocarbyls include: MAO, other aluminum sesquioxides, $R^0{}_3Al$, $R^0{}_2AlCl$, R^0AlCl_2 (wherein R^0 is alkyl), Grignard reagents, organolithium reagents, and diorganozinc reagents. Examples of suitable Lewis acids or Bronsted acids include: MAO, other aluminum sesquioxides, $R^0{}_3Al$, $R^0{}_2AlCl$, R^0AlCl_2 (wherein R^0 is alkyl), $B(C_6F_5)_3$, $R^{16}{}_3Sn[BF_4]$, H^+X^-, wherein X^- is a weakly coordinating anion, for example, tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, and Lewis acidic or Bronsted acidic metal oxides, for example, montmorillonite clay.

While not wishing to be bound by theory, the present inventors believe that the Lewis acid may be acting to further activate the catalysts provided herein via coordination to one or more of those heteroatoms which are not directly bound to the transition metal M, but which are π-conjugated to the nitrogens which are bound to the transition metal M. Substituents which contain additional Lewis basic groups, including, but not limited to, methoxy groups, positioned so as to further promote the binding of the Lewis acid at such π-conjugated heteroatoms, are also included in this invention. A nonlimiting example of secondary Lewis acid binding would include the following:



XLIII

wherein R^1, R^2, R^5, and R^6 are 2,6-dimethylphenyl; and X^- is a weakly coordinating anion.

The polymerizations may be conducted as solution polymerizations, as non-solvent slurry type polymerizations, as slurry polymerizations using one or more of the olefins or other solvent as the polymerization medium, or in the gas phase. One of ordinary skill in the art, with the present disclosure, would understand that the catalyst could be supported using a suitable catalyst support and methods known in the art. Substantially inert solvents, such as toluene, hydrocarbons, methylene chloride and the like, may be used. Propylene and 1-butene are excellent monomers for use in slurry-type copolymerizations and unused monomer can be flashed off and reused.

Temperature and olefin pressure have significant effects on polymer structure, composition, and molecular weight. Suitable polymerization temperatures are preferably from about −100 °C to about 200 °C, more preferably in the 20 °C to 150 °C range.

After the reaction has proceeded for a time sufficient to produce the desired polymers, the polymer can be recovered from the reaction mixture by routine methods of isolation and/or purification.

In general, the polymers of the present invention are useful as components of thermoset materials, as elastomers, as packaging materials, films, compatibilizing agents for polyesters and polyolefins, as a component of tackifying compositions, and as a component of adhesive materials.

High molecular weight resins are readily processed using conventional extrusion, injection molding, compression molding, and vacuum forming techniques well known in the art. Useful articles made from them include films, fibers, bottles and other containers, sheeting, molded objects and the like.

Low molecular weight resins are useful, for example, as synthetic waxes and they may be used in various wax coatings or in emulsion form. They are also particularly useful in blends with ethylene/vinyl acetate or ethylene/methyl acrylate-type copolymers in paper coating or in adhesive applications.

Although not required, typical additives used in olefin or vinyl polymers may be used in the new homopolymers and copolymers of this invention. Typical additives include pigments, colorants, titanium dioxide, carbon black, antioxidants, stabilizers, slip agents, flame retarding agents, and the like. These additives and their use in polymer systems are known *per se* in the art.

The molecular weight data presented in the following examples is determined at 135 °C in 1,2,4-trichlorobenzene using refractive index detection, calibrated using narrow molecular weight distribution poly(styrene) standards.

EXAMPLES

Other features of the invention will become apparent in the course of the following descriptions of exemplary embodiments which are given for illustration of the invention and are not intended to be limiting thereof.

Example1

Preparation of *N,N'*-bis(2,6-dimethylphenyl)oxalamide.

2,6-dimethylaniline, triethylamine, and dichloromethane were dried by passage through basic alumina. A 1 L round bottom flask, equipped with a magnetic stir bar and a 125 mL pressure-equalizing dropping funnel capped by a nitrogen inlet adapter, was charged with 53.38 g of 2,6-dimethylaniline, 250 mL of dichloromethane, and 44.76 g of triethylamine. A solution of 25.34 g of oxalyl chloride in 80 mL of dichloromethane was added dropwise under nitrogen with stirring and ice-bath cooling over 1.2 hours to give a thick paste which had to be occasionally swirled by hand to effect mixing. The mixture was allowed to stir at room temperature for 14 hours, then transferred to a separatory funnel, washed 3 times with water, separated and concentrated under reduced pressure (10 mm Hg) to give 63 g of crude solid. The crude product was dissolved in a boiling mixture of 1.30 L of toluene and 2.85 L of absolute ethanol, cooled to room temperature (about 23°C) and diluted with 260 mL of water, then allowed to crystallize for 16 hours. The resultant precipitate was isolated by vacuum filtration, washed with methanol (3 x 100 mL) and dried to give 39.1 g (66%) as white crystals. An additional 9.5 g (16.1%) was recovered from the filtrate by further dilution with approximately 500 mL of water. Field desorption mass spectrometry showed a parent ion peak at 296 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.29 (12 p, s), 7.15 (6 p, m), 8.86 (2 p, br s).

Example 2

Preparation of *N, N'*-bis(2,6-diisopropylphenyl)oxalamide.

2,6-Diisopropylaniline, triethylamine, and dichloromethane were dried by passage through basic alumina. A 1 L round bottom flask, equipped with a magnetic stir bar and a 125 mL pressure-equalizing dropping funnel capped by a nitrogen inlet adapter, was charged with 34.73 g of 2,6-diisopropylaniline (previously distilled), 180 mL of dichloromethane,

and 18.30 g of triethylamine. A solution of 10.57 g oxalyl chloride in 43 mL of dichloromethane was added dropwise under nitrogen with stirring and ice-bath cooling over 38 minutes to give a thick paste which had to be occasionally swirled by hand to effect mixing. The mixture was allowed to stir at room temperature (about 23° C) for 60 hours, then diluted with 700 mL of water to precipitate the product, which was isolated by filtration, washed with water and recrystallized from boiling isopropanol (4 L) to afford 22.38 g (66%) of white needles. Field desorption mass spectrometry showed a parent ion peak at 408 m/z. ^{1}H NMR (500 MHz, CD_2Cl_2, chemical shifts in ppm relative to TMS at 0 ppm): 1.22 (24 p, d, 6.8 Hz), 3.08 (4 p, septet, 6.8 Hz), 7.25 (4 p, d, 7.5 Hz), 7.37 (2 p, t, 7.5 Hz), 8.86 (2 p, br s).

Example 3

Preparation of *N, N'*-bis (4-methoxy-2,6-dimethylphenyl)oxalamide.

Triethylamine and dichloromethane were dried by passage through basic alumina. A 50 mL round bottom flask, equipped with a magnetic stir bar and a small pressure-equalized dropping funnel capped by a nitrogen inlet adapter, was charged with 1.5 g of 4-methoxy-2,6-dimethylphenylamine, 8 mL of dichloromethane, and 1.38 g of triethylamine. A solution of 0.39 of oxalyl chloride in 2 mL of dichloromethane was added dropwise under a nitrogen atmosphere with stirring and ice-bath cooling over 35 min. The mixture was allowed to stir at room temperature for 14 hours, then transferred to a separatory funnel, washed with water, separated and concentrated under reduced pressure (10 mm Hg) to give 1.75 g solids. The crude product was dissolved in 150 mL of boiling absolute ethanol and crystallized upon cooling to room temperature (about 23° C.). The resultant precipitate was isolated by vacuum filtration, and dried to give 1.39 g (86%) as white crystals. Field desorption mass spectrometry showed a parent ion peak at 356 m/z.

Example 4

Preparation of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride.

A 1 L round bottom flask was charged with 30.0 g of *N,N'*-bis(2,6-dimethylphenyl)oxalamide, 58.8 g of phosphorous pentachloride and 150 mL of dry toluene, and equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet adapter connected to a bubbler. The mixture was heated to reflux over 30 minutes, then maintained at reflux under nitrogen for another 95 minutes to give a yellow solution. Heating was discontinued and the mixture was allowed to cool to room temperature (about 23° C). A short path distillation adapter and receiving flask was attached in place of the condenser and the volatiles were removed under reduced pressure (1 mm Hg), initially at room temperature, then at 100° C, to give 20.1 g (60%) of a granular yellow solid. Field desorption mass spectrometry showed a parent ion peak at 332 m/z. ^{1}H NMR (300 MHz, C_6D_6, chemical shifts in ppm relative to TMS at 0 ppm): 2.04 (12 p, s), 6.91 (6 p, s).

Example 5

Preparation of N^1,N^2-bis(2,6-diisopropylphenyl)oxalodiimidoyl dichloride.

A 500 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet adapter connected to a bubbler was charged with 2.50 g of *N,N'*-bis(2,6-diispropylphenyl)oxalamide, 3.58 g of phosphorous pentachloride and 36 mL of dry toluene. The mixture was heated to reflux over 30 minutes, then maintained at reflux under nitrogen for another 210 minutes to afford a clear yellow solution. Heating was discontinued and the mixture was allowed to cool to room temperature (about 23° C). A short path distillation adapter and receiving flask were attached in place of the condenser and the volatiles were removed under reduced pressure (1 mm Hg), initially at room temperature, then at 100° C, to give a yellow oil, which slowly crystallized upon complete cooling. The product was purified by column

chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 3 v% ethyl acetate in hexane) to afford 1.49 g (55%) yellow crystals. Field desorption mass spectrometry showed a parent ion peak at 444 m/z.

Example 6

Preparation of N^1,N^2-bis(4-methoxy-2,6-dimethylphenyl)oxalodiimidoyl dichloride.

A 50 mL round bottom flask was charged with 1.37 g of *N,N'*-bis(4-methoxy-2,6-dimethylphenyl)oxalamide 1.88 g of phosphorous pentachloride and 15 mL of dry toluene, and equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet adapter connected to a bubbler. The mixture was heated, with stirring, at about 100° C until the evolution of HCl ceased. Then, another 0.22 g PCl_5 was added and the mixture was heated another 30 min at 80° C. After cooling to room temperature the mixture was transferred to a separatory funnel, and some crystallization occurred upon transfer. Complete transfer and re-dissolution of the product was accomplished by the addition of dichloromethane. The organic layer was washed with saturated aqueous sodium bicarbonate, then concentrated *in vacuo* to afford 1.44 g crystalline yellow solid. Field desorption mass spectrometry showed a parent ion peak at 392 m/z.

Example 7

Preparation of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 504 mg of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 136 mg of sodium hydride (60% mineral oil dispersion), 4.0 mL of dry tetrahydrofuran and 0.140 mL of 1,2-ethanedithiol. The mixture was heated at reflux for 2 hours, after which another 66 mg of sodium hydride dispersion was added and the mixture was refluxed for an additional hour. After cooling, the mixture was diluted with water and diethyl ether, and the ether layer was separated, washed again with water, and dried with magnesium sulfate to

afford a yellow-orange oil. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 15 v% of ethyl acetate in hexane) afforded 296 mg of a yellow oil which was crystallized by addition of hexane and collected by vacuum filtration to give 219 mg of yellow granular crystals. Field desorption mass spectrometry showed a parent ion peak at 354 m/z. ^1H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.17 (12p, s), 3.27 (4p, br s), 6.4-7.12 (6 p, m).

Example 8

Preparation of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane.

A 250 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by an argon inlet was sequentially charged with 0.69 g of a 60% dispersion of sodium hydride in mineral oil, 3.34 g of *N*[1],*N*[2]-bis(2,6-diisopropylphenyl)oxalodiimidoyl dichloride, 20 mL of dry tetrahydrofuran, and 0.70 mL of 1,2-ethanedithiol. The mixture was heated under argon at reflux for 3 hours, after which another 0.25 g of sodium hydride dispersion was added and the mixture was refluxed for an additional 2.5 hours. After cooling, the mixture was diluted with water and diethyl ether, and the ether layer was separated, washed with water, and dried with magnesium sulfate to afford a yellow-orange oil. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 10 v% ethyl acetate in hexane) afforded 3.14 g of a yellow-orange glass. Field desorption mass spectrometry showed a parent ion peak at 466 m/z. ^1H NMR (500 MHz, CD_2Cl_2, chemical shifts in ppm relative to TMS at 0 ppm): 1.10-1.22 (12 p, m), 1.22-1.40 (12 p, m), 2.78-3.05 (4 p, m), 3.30 (4 p, br s), 7.05-7.25 (6 p, m).

Example 9

Preparation of 2,3-bis(phenylimino)-[1,4]dithiane.

A 250 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by an argon inlet was sequentially charged with 0.69 g of a 60% dispersion of sodium hydride in mineral oil, a freshly

prepared solution of 2.08 g N^1,N^2- diphenyloxalodiimidoyl dichloride in 20 mL of dry tetrahydrofuran, and 0.70 mL of 1,2-ethanedithiol. The mixture was heated under argon at reflux for 2 hours, after which another 0.30 g of sodium hydride dispersion was added and the mixture refluxed for an additional 3 hours. After cooling, the mixture was diluted with water and diethyl ether, and the ether layer was separated, washed with water, and dried with magnesium sulfate to afford a yellow-orange gummy solid. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 10 v% ethyl acetate in hexane) afforded 296 mg of a yellow oil which was crystallized by addition of hexane to give 0.161 g of yellow-orange granular crystals. Field desorption mass spectrometry showed a parent ion peak at 298 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 3.27 (4p, br s), 7.02 (4p, apparent d, 8.1 Hz), 7.19 (2p, apparent t, 7.2 Hz), 7.40 (4p, apparent t, 7.8 Hz).

Example 10

Preparation of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydrobenzo[1,4]dithiine.

A 100 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by an argon inlet was sequentially charged with 0.294 g of a 60% dispersion of sodium hydride in mineral oil, 4 mL of dry tetrahydrofuran, and 0.253 g of 1,2-benzenedithiol. After the bubbling had subsided, 0.600 g of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride was added. The mixture was stirred at 25° C. for 45 minutes, then heated to reflux over 15 minutes and held at reflux for 1 hour. After cooling, the mixture was diluted with water and diethyl ether, and the ether layer was separated, washed with water, and dried with magnesium sulfate, and concentrated *in vacuo* to give a yellow-orange oil. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 2 v% ethyl acetate in hexane) afforded 0.412 g of a yellow-orange glass. Field desorption mass spectrometry showed a parent ion peak at 402 m/z. ^{1}H

NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.16 (12 p, s), 7.01-7.24 (10 p, m).

Example 11

Preparation of 2,3- bis(4-methoxy-2,6-dimethylphenylimino)-[1,4]dithiane.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 420 mg of N^1,N^2-bis(4-methoxy-2,6-dimethylphenyl)oxalodiimidoyl dichloride. To a 50 mL pear flask was added 171 mg of sodium hydride (60% mineral oil dispersion), 1.75 mL of dry tetrahydrofuran, and, cautiously, 0.11 mL ethane dithiol. The resulting mixture was syringed into the N^1,N^2-bis(4-methoxy-2,6-dimethylphenyl)oxalodiimidoyl dichloride solution using 5 mL dry THF to complete the transfer. The reaction flask was heated at reflux for 3 hours, after which another 45 mg of sodium hydride dispersion and another 20 μL ethane dithiol was added and the mixture was refluxed for an additional hour. After cooling, the mixture was diluted with water and diethyl ether, and the ether layer was separated, washed again with water, dried with magnesium sulfate, and concentrated to afford a yellow-orange solid. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 15 v% ethyl acetate in hexane) afforded 147 mg of a yellow powder. Field desorption mass spectrometry showed a parent ion peak at 414 m/z.

Example 12

Preparation of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 504 mg of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 66 mg of sodium hydride (60% mineral oil dispersion), 5.0 mL of dry tetrahydrofuran, 0.230 mL of triethylamine (dried by passage through alumina) and 0.093 mL of dry ethylene glycol. The mixture was heated at reflux for 105 minutes, after which another 66 mg of sodium hydride dispersion was added and the mixture was refluxed for an additional hour. After cooling, the mixture was

diluted with water and diethyl ether, and the ether layer was separated, washed again with water, dried with magnesium sulfate, and concentrated to afford a yellow oil. Crystallization from heptane gave rosettes of off-white crystals (225 mg, 1st crop). Field desorption mass spectrometry showed a parent ion peak at 322 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.20 (12 p, s), 4.35 (4 p, s), 6.94 (2 p, m), 7.05 (4 p, m).

Example 13

Preparation of 5-methoxymethyl-2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by an argon inlet was charged with 504 mg of *N*^{1},*N*^{2}-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 155 mg of sodium hydride (60% mineral oil dispersion), 3.5 mL of dry tetrahydrofuran and 188 mg of 3-methoxy-1,2-propanediol. The mixture was heated to reflux over 10 min and held at reflux for 2 hours. After cooling, the mixture was diluted with diethyl ether, and washed with water (2 x 100 mL), and dried with magnesium sulfate and concentrated *in vacuo* to afford 329 mg of a yellow oil. Column chromatography (SiO_2, Merck Grade 9385 230–400 mesh, 60 Å; 20 v% of ethyl acetate in hexane) afforded 216 mg of a glassy yellow solid. Field desorption mass spectrometry showed a parent ion peak at 366 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.18 (12 p, s), 3.31 (3 p, s), 3.45-3.65 (2 p, m), 4.20–4.40 (2 p, m), 4.40–4.55 (1 p, m), 6.80-7.15 (6 p, m).

Example 14

Preparation of 2,3-bis(benzyloxymethyl)-5,6-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 100 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by an argon inlet was charged with 265 mg of sodium hydride (60% mineral oil dispersion), 7.5 mL of dry tetrahydrofuran,

1.0 g of 3-methoxy-1,2-propanediol and 1.0 g of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride. The yellow mixture was heated to reflux over 15 min and became very viscous. More tetrahydrofuran (5 mL) was added and the mixture was stirred with a glass rod, then heated for another 30 min. Next, an additional 220 mg of sodium hydride (60% mineral oil dispersion) and an additional 10 mL tetrahydrofuran were added. Most of the yellow color was discharged with the second addition of sodium hydride, rendering the very viscous reaction mixture light brown. Heating was continued for about 15 min more, and after cooling, the mixture was diluted with diethyl ether and washed with water to remove the sodium chloride. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 2 v% of ethyl acetate in hexane) afforded a beige gummy solid. Field desorption mass spectrometry showed a parent ion peak at 562 m/z. ^1H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.17 (12 p, s), 3.63 (4 p, br s), 4.38 (2 p, d, 12.6 Hz), 4.47 (2 p, d, 12.6 Hz), 4.56 (2 p, br s), 6.85-7.4 (16 p, m).

Example 15

Preparation of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 1.0 g of N^1,N^2-bis(2,6-diisopropylphenyl)oxalodiimidoyl dichloride, 268 mg of sodium hydride (60% mineral oil dispersion), 4.0 mL of dry tetrahydrofuran, and 212 mg of dry ethylene glycol. Under an argon atmosphere, the mixture was heated to 65° C held at that temperature for 90 minutes. The mixture was then quickly heated to reflux and held at reflux for 30 minutes more. After cooling, the mixture was diluted with 50 mL diethyl ether, and washed with water, dried with magnesium sulfate, and concentrated *in vacuo* to afford a light straw-yellow oil (903 mg). Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 8 v% ethyl acetate in hexane) afforded 257 mg of a pale green glass. Field desorption mass spectrometry showed

a parent ion peak at 434 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 1.24 (24 p, d, 6.6 Hz), 3.00 (4p, septet, 6.6 Hz), 4.31 (4 p, br s), 7.04-7.20 (6 p, m).

Example 16

Preparation of 2,3-bis(2,6-dimethylphenylimino)-4-methylmorpholine.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet adapter was charged with 503 mg of *N*^{1},*N*^{2}-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 346 mg triethylamine, 4 mL dry, deoxygenated toluene, and 0.135 mL 2-(methylamino)ethanol. The mixture was heated to reflux under nitrogen over 30 minutes and maintained at reflux for another 4.25 hours. After cooling, the mixture was diluted with 45 mL diethyl ether and washed three times with water (110 mL total). The ether extract was dried with magnesium sulfate, filtered and concentrated under reduced pressure (10 mm Hg) to give a light-colored solid (512 mg). Recrystallization from heptane/dichloromethane gave 138 mg pale off-white crystals (first crop). Field desorption mass spectrometry showed a parent ion peak at 335 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 1.73 (6 p, s), 2.10 (6 p, s), 3.27 (3 p, s), 3.55-3.65 (2 p, m), 4.16-4.26 (2 p, m), 6.65-6.95 (6 p, m).

Example 17

Preparation of 2,3-bis(2,6-diisopropylphenylimino)-4-methylmorpholine.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet adapter was charged with 725 mg of *N*^{1},*N*^{2}-bis(2,6-diisopropylphenyl)oxalodiimidoyl dichloride, 143 mg of sodium hydride (60% mineral oil dispersion), 4 mL dry tetrahydrofuran, and 0.144 mL 2-(methylamino)ethanol. The mixture was stirred at room temperature for 4 hours, and allowed to stand at room temperature for another 5 days. The mixture was diluted with diethyl ether and washed water. The ether extract was concentrated under reduced pressure (10 mm

Hg) to give a yellow oil which partially crystallized over several hours). Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 12 v% of ethyl acetate in hexane) afforded 156 mg light yellow crystalls. Field desorption mass spectrometry showed a parent ion peak at 447 m/z. ^1H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 0.86 (6 p, d, 7.2 Hz), 1.04 (6 p, d, 7.2 Hz), 1.15 (6 p, d, 7.2 Hz), 1.18 (6 p, d, 7.2 Hz), 2.27 (2 p, apparent septet, 7.2 Hz), 2.97 (2 p, apparent septet, 7.2 Hz), 3.28 (3 p, br s), 3.55-3.65 (2 p, m), 4.14-4.22 (2 p, m), 6.80-7.02 (6 p, m).

Example 18

Preparation of 1,3-bis-(2,6-dimethyl-phenyl)-4,5-bis-(2,6-dimethyl-phenylimino)-imidazolidin-2-one.

In a 250 mL round bottom flask, 1.0 g of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine was dissolved in 35 mL dry, deoxygenated dichloromethane while stirring under an argon atmosphere. 0.67 mL dry triethylamine was added, followed by 240 mg triphosgene. With the addition of the triphosgene, the color shifted from pale yellow to chrome yellow. The mixture was allowed to stir for 16 h at room temperature, after which time an additional 460 mg of triphosgene was added. After about 15 min, 10 mg dimethylamino pyridine and an additional 240 mg triphosgene were added. After about 15 min more, another 220 mg triphosgene and about 0.5 g dimethylamino pyridine were added. The mixture was washed with saturated aqueous sodium bicarbonate, then with water, and then concentrated *in vacuo* to afford a yellow powder. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 4 v% ethyl acetate in hexane) afforded 763 mg of a chrome yellow powder. Field desorption mass spectrometry showed a parent ion peak at 528 m/z. ^1H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.01 (12 p, s), 2.32 (12 p, s), 6.4-7.3 (12 p, m).

Example 19

Preparation of 1,3-bis(4-methoxy-2,6-dimethylphenyl)-4,5-bis-(4-methoxy-2,6-dimethylphenylimino)imidazolidin-2-one.

A 100 mL round bottom was equipped with a magnetic stirrer and charged with 0.75 mL dry triethylamine, 6 mL dry and deoxygenated dichloromethane, and 0.335 g N^1,N^2,N^3,N^4-tetrakis(4-methoxy-2,6-dimethylphenyl)oxalamidine. With stirring, 178 mg triphosgene was added, and the flask was quickly capped with a septum. A precipitate formed and the color shifted from yellow to orange. After 2.5 days another 78 mg triphosgene was added, and the reaction left to stir another 2 hours. 150 mg more triphosgene was added, and the reaction left to stir for another 16 hrs. The reaction mixture was diluted with 50 mL diethyl ether and washed with water (2 x 50 mL). The aqueous washings were back-extracted with dichloromethane. The organic layers were combined and dried over magnesium sulfate, and concentrated *in vacuo* to afford an orange oil. Upon addition of diethyl ether to the oil, small orange crystals formed. The compound was isolated on a vacuum filter and washed with diethyl ether to afford 216 mg yellow-orange microcrystalline powder. Field desorption mass spectrometry showed a parent ion peak at 648 m/z. ^{1}H NMR (500 MHz, CD_2Cl_2, chemical shifts in ppm relative to TMS at 0 ppm): 1.98 (12 p, broad hump), 2.25 (12 p, broad hump), 3.63 (6 p, broad hump), 3.75 (6 p, broad hump), 6.32 (4 p, broad hump), 6.59 (4 p, broad hump).

Example 20

Preparation of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine.

A 1 L round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 5.6 g of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 43 mL of dry toluene and 32.7 g of 2,6-dimethylaniline (dried by passage through alumina). The mixture was heated to reflux under nitrogen over 30 minutes, then maintained at reflux another 3 hours. After cooling, the mixture was

diluted with 206 g of absolute ethanol and 45 g of water to produce copious amounts of precipitate. Isolation by vacuum filtration, with ethanol (600 mL) and heptane (600 mL) washes, and subsequent drying, gave 6.1 g (72%) as pale yellow crystals. Field desorption mass spectrometry showed a parent ion peak at 502 m/z. ^1H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 2.16 (24 p, s), 6.75 (12 p, s), 8.6 (2 p, br s).

Example 21

Preparation of N^1,N^2,N^3,N^4-tetrakis(4-methoxy-2,6-dimethylphenyl)oxalamidine.

A 500 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 1.0 g of N^1,N^2-bis(4-methoxy-2,6-dimethylphenyl)oxalodiimidoyl dichloride, 24 mL of dry toluene and 854 mg of 4-methoxy-2,6-dimethylphenylamine, and 0.90 mL triethylamine (dried by passage through alumina). The mixture was heated to reflux under nitrogen over 30 minutes, then maintained at reflux another 14 hours. After cooling, the mixture was diluted with dichloromethane and washed with water. The impure compound was adsorbed onto SiO_2, and column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 12.5 v% ethyl acetate in hexane) afforded 340 mg of a yellow powder. Field desorption mass spectrometry showed a parent ion peak at 622 m/z.

Example 22

Preparation of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine.

A 25 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet adapter was charged with 0.50 g of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 1.1 mL of *N*,*N'*-dimethylethylenediamine and 4.0 mL of dry toluene. The mixture was heated to reflux under nitrogen over 15 minutes and maintained at reflux for another 30 minutes. After cooling, the mixture was diluted with diethyl ether and washed three times with water. The ether extract was dried with magnesium sulfate, filtered and concentrated under reduced pressure (10

mm Hg) to give a yellow solid (0.50 g). Recrystallization from heptane gave pale yellow crystals. Field desorption mass spectrometry showed a parent ion peak at 348 m/z. ^1H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 1.83 (br s, 12 p), 2-3.4 (two very broad humps, 4 p), 3.42 (br s, 6 p), 6.66 (t, 2p), 6.84 (d, 4p).

Example 23

Preparation of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 100 mg of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 79 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) was added and the mixture was stirred under an argon atmosphere, turning red-brown within about 5 minutes and slowly producing a red-brown crystalline precipitate. After 1 hour, another 5 mL of dichloromethane was added. The mixture was stirred another 21 hours at 21° C, then diluted with 10 mL of dry, deoxygenated hexane and stirred another 8 hours. The supernatant was removed via a filter paper-tipped cannula, and the residue dried *in vacuo* at 1 mm Hg to afford 116 mg of red-brown crystals.

Example 24

Preparation of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane.

A Schlenk flask equipped with a magnetic stir bar was charged with 79 mg of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane (0.17 mmol) and 49 mg of (1,2-dimethoxyethane)nickel(II) dibromide (0.16 mmol)under an argon atmosphere. Dry, deoxygenated dichloromethane (15 mL) was added and the mixture was stirred under an argon atmosphere, turning red-brown within about 10 minutes. After 2 hours, the CH_2Cl_2 was removed *in vacuo*. The resulting red-brown solid was washed with 2x10 mL of hexane

and the solid was dried *in vacuo* for several hours affording 76 mg of a brown solid.

Example 25

Preparation of the nickel dibromide complex of 2,3-bis(phenylimino)-[1,4]dithiane.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 151 mg of 2,3-bis(phenylimino)-[1,4]dithiane and 123 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (10 mL) was added and the mixture was stirred under an argon atmosphere, turning dark brown within about 5 minutes and slowly producing a red-brown crystalline precipitate. After 80 minutes, the mixture was concentrated to apparent dryness under a stream of argon, then further dried *in vacuo* for 1 hour at 50 mTorr to afford a red-brown powder.

Example 26

Preparation of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydrobenzo[1,4]dithiine.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 110 mg of 2,3-bis-(2,6-dimethylphenylimino)-2,3-dihydrobenzo[1,4]dithiine and 71 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (8 mL) was added and the mixture was stirred under an argon atmosphere, quickly turning red-brown. The mixture was stirred for 1 hour, concentrated to dryness under a stream of argon, then further dried *in vacuo* for 1 hour at 50 mTorr to yield a red-brown crystalline powder.

Example 27

Preparation of the nickel dibromide complex of 2,3- bis(4-methoxy-2,6-dimethylphenylimino)-[1,4]dithiane.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 147 mg of 2,3- bis(4-methoxy-2,6-dimethylphenylimino)-[1,4]dithiane and 93 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (10 mL) was added and the mixture was stirred under an argon atmosphere, turning dark brown almost immediately, and producing a brown precipitate. After 2 hours, 10 mL dry and deoxygenated hexane was added to complete the precipitation. The supernatant was removed via filter paper-tipped cannula, the residue dried *in vacuo* (0.5 mm Hg) for 14 h to obtain the product as a brown microcrystalline solid.

Example 28

Preparation of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 100 mg of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane and 87 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) was added and the mixture was stirred under an argon atmosphere, slowly producing a brown crystalline precipitate. After 1 hour, another 5 mL of dichloromethane was added. The mixture was stirred another 21 hours at 21° C, then diluted with 10 mL of dry, deoxygenated hexane and stirred another 8 hours. The supernatant was removed via a filter paper-tipped cannula, and the residue dried *in vacuo* at 1 mm Hg to afford 117 mg of brown crystals.

Example 29

Preparation of the nickel dibromide complex of 2,3-bis(benzyloxymethyl)-5,6-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 172 mg of 2,3-bis(benzyloxymethyl)-5,6-bis(2,6-dimethylphenylimino)-[1,4]dioxane and 85 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (12 mL) was added and the mixture was stirred under an argon atmosphere, almost immediately turning red-brown. After 1.75 hours, the mixture was concentrated dryness under a stream of argon for 16 h, then further dried *in vacuo* to afford 182 mg of a red-brown crystalline powder.

Example 30

Preparation of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-4-methylmorpholine.

A 25 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 100 mg of 2,3-bis(2,6-dimethylphenylimino)-4-methylmorpholine and 84 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) was added and the mixture was stirred under an argon atmosphere for 1 hour, after which another 5 mL dichloromethane was added. After 16 hours, the mixture was diluted with 10 mL hexane, and the supernatent was removed via a filter paper tipped cannula, and the residue was dried *in vacuo* to obtain 139 mg green crystals.

Example 31

Reaction of 1,3-bis-(2,6-dimethyl-phenyl)-4,5-bis-(2,6-dimethyl-phenylimino)-imidazolidin-2-one, (1,2-dimethoxyethane)nickel(II) dibromide, and silver tetrafluoroborate.

In an argon filled glove box, a flame-dried Schlenk flask equipped with a magnetic stir bar was charged with 159.6 mg of 1,3-bis-(2,6-dimethyl-phenyl)-4,5-bis-(2,6-dimethyl-phenylimino)-imidazolidin-2-one and 92.7 mg of (1,2-dimethoxyethane)nickel(II) dibromide and 59.4 mg silver tetrafluoroborate. The flask was wrapped in aluminum foil, and on the Schlenk line, under an argon atmosphere, 10 mL dry tetrahydrofuran was added. A white precipitate immediately separated. The mixture was stirred for 25 min, then the supernatant was transferred via filter paper-tipped cannula to a dry septum-capped vial. The supernatant was concentrated to dryness under a stream of dry argon for 16 h to afford 256 mg of a yellow crystalline powder.

Example 32

Preparation of the nickel dibromide complex of 1,3-bis(4-methoxy-2,6-dimethylphenyl)-4,5-bis(4-methoxy-2,6-dimethylphenylimino)imidazolidin-2-one.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 101 mg of 1,3-bis(4-methoxy-2,6-dimethylphenyl)-4,5-bis(4-methoxy-2,6-dimethylphenylimino)imidazolidin-2-one and 40 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (10 mL) was added and the mixture was stirred under an nitrogen atmosphere, slowly turning dark red-brown over 3 hours. After 2 more hours, the supernatant was removed to a flame-dried Schlenk flask via a filter paper-tipped cannula, diluted with 10 mL dry, deoxygenated hexane, and concentrated to dryness under a stream of nitrogen to give a mixture of a tan microcrystalline powder and

large, well-defined dark brown crystals. The latter were separated and used without further purification.

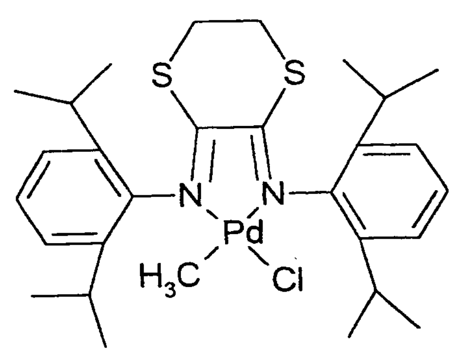
Example 33

Preparation of the nickel dibromide complex of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 48 mg of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine and 35 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) was added and the mixture was stirred under an argon atmosphere, turning green within about 5 minutes and slowly producing a green precipitate. After a total of 7 hours, the volatiles were removed under reduced pressure (1 mm Hg) and the residue was washed with 2 x 5 mL of dry, deoxygenated diethyl ether. The resultant green solid was dried under reduced pressure (1 mm Hg).

Example 34

Synthesis of:

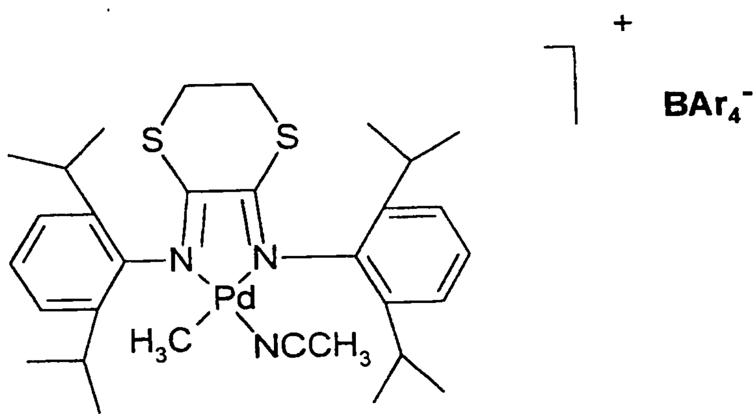


In the glove box, a Schlenk flask was charged with 500 mg of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane and 250 mg (1,5-cyclooctadiene)palladium methyl chloride. The flask was removed form the box and placed under an argon atmosphere. To the solid mixture was added 20 ml of methylene chloride resulting in an orange solution. The

mixture was left to stir for 4 hours. After 4 hours, 20 ml of hexane was added resulting in the precipitation of an orange solid. The solvent was removed via filter cannula leaving a red/orange solid. The solid was subsequently washed 3 x 10 ml of hexane and dried *in vacuo* resulting in 490 mg of the complex (83 % yield). ^{1}H NMR is consistent with the proposed structure.

Example 35

<u>Synthesis of:</u>



XXXV

In the glove box, a Schlenk flask was charged with 490 mg of 2,3-bis(2,6-diisopropylphenylimino)[1,4]dithiane palladium methyl chloride and 738 mg of $NaBAr_4$ where Ar =3,5-bis-triflurometh ylphenyl. The flask was

removed form the box and placed under an argon atmosphere. To the solid mixture was added 25 ml of methylene chloride and 0.2 ml of acetonitrile resulting in an orange solution. The mixture was left to stir for 3 hours. After 3 hours, the solution was transfered via filter cannula leaving a gray solid (NaCl). The solvent was subsequently removed *in vacuo* resulting in a orange glass (1.1 g of the complex, 90 % yield). ^1H NMR is consistent with the proposed structure.

Example 36

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 5.3 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The resultant suspension was cooled to 0 °C and allowed to equilibrate with 1 atmosphere ethylene for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. A white polyethylene precipitate (with a faint red-brown tinge) was observed within minutes. After 10 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.05-0.1 mm Hg) for 48 hours to give 2.5 g of a white polyethylene. A similar reaction at 21.5° C using 0.104 mg of the nickel complex (100 µL of a 1.04 mg/mL stock solution in *o*-difluorobenzene) gave 426 mg polyethylene after 14 minutes reaction (359,000 Turnovers per hour (TO/h)). ^1H NMR: 24 branches/1000 carbon atoms. GPC: M_n = 810,000; M_w/M_n = 2.3.

Exampl 37

Polymerization of ethylene using a catalyst generated *in situ* from 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane, bis(1,5-cyclooctadiene)nickel(0) and $HB(Ar)_4$ (Ar = 3,5-bis(trifluoromethyl)phenyl).

A 250 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 20 mg of bis(1,5-cyclooctadiene)nickel(0), 33 mg of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane, and 83 mg of the ether solvate $HB(Ar)_4$. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The deep violet solution which resulted was stirred under ethylene at 25 °C for 30 minutes, then quenched by addition of acetone (50 mL), and methanol (50 mL). The polyethylene which separated was isolated by vacuum filtration and washed with acetone, then dried under reduced pressure (0.5 mm Hg) for 18 hours to give 339 mg of white polyethylene (332 TO/h). ^1H NMR: 47 branches/1000 carbon atoms. GPC: M_n = 180,000; M_w/M_n = 2.4.

Example 38

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar was charged with 0.5 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The flask was evacuated and refilled with ethylene, and charged with 75 mL of dry, deoxygenated toluene. The reaction flask was placed in a water bath (23° C) and treated with 1.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. A white polyethylene precipitate was observed within seconds. After 5 minutes, the mixture was quenched by the addition of acetone, methanol and 6 N aqueous HCl. The swollen polyethylene which separated was isolated by vacuum filtration and washed with acetone. The resulting

polymer was dried for several hours in a vacuum oven at 80° C. 580 mg of a white rubbery solid was isolated (285,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 87° C. ^{1}H NMR, 37 branches/1000 carbon atoms. GPC: M_n = 186,000; M_w/M_n = 2.06.

Example 39

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar was charged with 0.5 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane. The flask was evacuated and refilled with ethylene, and charged with 75 mL of dry, deoxygenated toluene. The reaction flask was placed in a water bath and treated with 1.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. After 10 minutes, the mixture was quenched by the addition of acetone, methanol and 6 N aqueous HCl. The swollen polyethylene which separated was isolated by vacuum filtration and washed with acetone. The resulting polymer was dried for several hours in a vacuum oven at 80° C. 210 mg of a white rubbery amorphous polymer was isolated (63,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 6 °C. ^{1}H NMR: 92 branches/1000 carbon atoms. GPC: M_n = 146,000; M_w/M_n = 1.85.

Example 40

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MMAO (modified methylaluminoxane; 23 % iso-butylaluminoxane).

A 600 mL Parr® autoclave was first heated to about 100° C under high vacuum to ensure that the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.3 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-

dimethylphenylimino)-[1,4]dithiane. The autoclave was heated to 40° C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig with ethylene and the temperature ramped up to 50° C. After 10 minutes at 50° C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated and dried for several hours in a vacuum oven at 80° C. 4.8 g of a white rubbery solid was isolated (2,000,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 97 °C. ^{1}H NMR: 28 branches/1000 carbon atoms. GPC: M_n = 155,000; M_w/M_n = 2.10.

Example 41

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane).

A 600 mL Parr® autoclave was first heated to about 100° C under high vacuum to ensure that the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.3 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The autoclave was cooled to 15° C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig with ethylene and the temperature ramped up to 25° C. After 10 minutes at 25° C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated and dried for several hours in a vacuum oven at 80° C. 4.4 g of a white rubbery polyethylene was isolated (1,800,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 125 °C. ^{1}H NMR: 6 branches/1000 carbon atoms. GPC: M_n = 598,000; M_w/M_n = 2.12.

Example 42

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane).

A 600 mL Parr® autoclave was first heated to about 100° C under high vacuum to ensure that the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 1.0 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The autoclave was heated to 55° C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig with ethylene and the temperature ramped up to 65° C. After 10 minutes at 65° C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated and dried for several hours in a vacuum oven at 80° C. 5.3 g of a white rubbery solid was isolated (640,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 78° C. ^{1}H NMR: 47 branches/1000 carbon atoms. GPC: M_n = 86,000; M_w/M_n = 1.95.

Example 43

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane).

A 600 mL Parr® autoclave was first heated to about 100° C under high vacuum to ensure that the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 1.0 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The autoclave was heated to 70° C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig with ethylene and the temperature

ramped up to 80° C. After 10 minutes at 80°C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated and dried for several hours in a vacuum oven at 80° C 3.5 g of a white rubbery solid was isolated (440,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 67° C. ^{1}H NMR: 53 branches/1000 carbon atoms. GPC: M_n = 87,000; M_w/M_n = 1.66.

Example 44

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane).

A 600 mL Parr® autoclave was first heated to about 100° C under high vacuum to ensure that the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.5 mL of a stock solution (10 mg in 10 mL CH2Cl2) of the nickel dibromide complex of 2,3-bis(2,6-di-iso-propylphenylimino)-[1,4]dithiane. The autoclave was heated to 40° C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig with ethylene and the temperature ramped up to 50° C. After 10 minutes at 50° C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated and dried for several hours in a vacuum oven at 80° C. 2.4 g of a white rubbery solid was isolated (700,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 46° C. 1H NMR: 75 branches/1000 carbon atoms. GPC: M_n = 966,000; M_w/M_n = 1.70.

Example 45

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane.

The procedure described in example 44 was followed except the polymerization was conducted at 80 °C. 1.4 g of a white rubbery solid was

isolated (400,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 0° C. ^{1}H NMR: 95 branches/1000 carbon atoms. GPC: M_n = 406,000; M_w/M_n = 2.05.

Example 46

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in Example 44 was followed except the polymerization was conducted at 65° C. 2.15 g of a white rubbery solid was isolated (630,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 15° C. ^{1}H NMR: 89 branches/1000 carbon atoms. GPC: M_n = 502,000; M_w/M_n = 1.78.

Example 47

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of MMAO(23 % iso-butylaluminoxane.

The procedure described in Example 44 was followed except the polymerization was conducted at 25 ° C. 1.9 g of a white rubbery solid was isolated (560,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 90 °C. ^{1}H NMR: 33 branches/1000 carbon atoms. GPC: M_n = 839,000; M_w/M_n = 1.37.

Example 48

Oligomerization of ethylene to α-olefin with the nickel dibromide complex of 2,3-bis(phenylimino)-[1,4]dithiane in the presence of MAO.

A 1 L Fischer-Porter bottle was assembled onto a pressure head equipped with a mechanical stirrer and gas and liquid feed-through ports, then pressurized to 75 psig of ethylene and relieved to ambient pressure seven times. The bottle was immersed in a 21.5° C. water bath, then 50 mL

of dry, deoxygenated toluene was added via syringe, followed by 100 μL of a stock solution of 15.3 mg of the nickel dibromide complex of 2,3-bis(phenylimino)-[1,4]dithiane in 15.0 mL of dichloromethane, followed by another 50 mL of toluene. The mixture was stirred at 300 rpm under 75 psig ethylene for 5 minutes to saturate the solution with ethylene, then the pressure was relieved, and 4.0 mL of a 10 wt% solution of MAO in toluene was quickly added. The flask was immediately re-pressurized to 75 psig ethylene and stirred at 300 rpm. After 30 minutes, the pressure was relieved and the reaction quenched by addition of 10 mL of methanol. After disassembling the apparatus, another 40 mL of methanol, 50 mL of 6 N aqueous HCl, and 10 mL acetone were added and the mixture was stirred to complete hydrolysis of the MAO. The resultant organic layer was separated, washed with 6 N aqueous HCl (1 x 25 mL), and water (2 x 50 mL), then concentrated under reduced pressure (15 Torr) at 40° C to obtain an oil. This was treated with toluene (50 mL) and re-concentrated twice, then treated with acetone (50 mL) and re-concentrated, to obtain a waxy white polyethylene solid. Drying *in vacuo* at 100° C, 250 mm Hg for 14 hours gave 0.180 g of polymer, approximate M_n = 517, containing approximately 85% α-olefin and 15% internal olefin.

Example 49

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydrobenzo[1,4]dithiine in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 100 mL of dry, deoxygenated toluene. The flask was placed in a water bath and allowed to equilibrate with 1 atmosphere ethylene for 10 minutes, then 0.25 mL of a stock solution prepared from 10.2 mg of the nickel dibromide complex of 2,3-bis-(2,6-dimethylphenylimino)-2,3-dihydrobenzo[1,4]dithiine in 13.11 g

dry deoxygentated dichloromethane was added. The reaction mixture was then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. Ethylene uptake and formation of a polyethylene precipitate were observed. After 6.5 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration, then dried at 80° C *in vacuo* for several hours. 287 mg of a white powdery polyethylene was isolated (236,000 TO/h). DSC (2nd heat) melt with an endothermic maximum at 88° C. ^1H NMR showed this material to contain approximately 36 branches/1000 carbon atoms GPC: M_n = 145,000; M_w/M_n = 2.35.

Example 50

Polymerization of ethylene using a catalyst formed in situ from 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane and $[Pd(NCCH_3)_4][BF_4]_2$.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 0.022 g of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane and 0.019 g $[Pd(NCCH_3)_4][BF_4]_2$. The flask was evacuated and refilled with ethylene, then 100 mL of dry, deoxygenated dichloromethane was added via syringe and the resultant mixture was stirred under 1 atmosphere of ethylene at 25° C. Very little ethylene uptake was observed. After 10 minutes, 0.412 g $B(C_6F_5)_3$ was added, resulting in an increased rate of ethylene uptake. After a total of 84 minutes, the reaction was worked up by evaporating the dichloromethane under a stream of nitrogen, washing the residue with methanol repeatedly to extract the $B(C_6F_5)_3$, and drying the residue *in vacuo* to obtain 0.57 g of amorphous polyethylene, approximate M_n = 17,000; M_n/M_w = 1.3. ^1H NMR showed approximately 105 branches per 1000 carbons.

Example 51

Polymerization of ethylene with the nickel dibromide complex of 2,3- bis(4-methoxy-2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.

A 500 mL round bottom flask fitted with a Schlenk adapter and equipped with a magnetic stir bar and capped with a septum was evacuated, flame-dried, then refilled with ethylene. The flask was provided with a room temperature (ca. 23°C) water bath, then charged with 100 mL of dry, deoxygenated toluene and allowed to equilibrate with 1 atmosphere ethylene for 30 minutes. The reaction mixture was then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene, then 0.10 mL of a stock solution (prepared from 6.3 mg of the nickel dibromide complex of 2,3- bis(4-methoxy-2,6-dimethylphenylimino)-[1,4]dithiane and 6.5 mL dichloromethane) was added. After 10 minutes, the reaction mixture was quenched by the addition of acetone, methanol and 6 N aqueous HCl. The polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, dried on the filter for 2 h, then further dried 13 days in a vacuum oven at 80°C. 182 mg of a white polyethylene was isolated (254,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 124° C. ^{1}H NMR: 13 branches/1000 carbon atoms. GPC: M_n =145,600; M_w/M_n =2.6.

Example 52

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of $(CH_3CH_2)_2AlCl$.

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.5 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane. The autoclave was heated to 45 °C and 2 mL of $(CH_3CH_2)_2AlCl$ (5000 equiv.) in toluene was added. The

reactor was rapidly pressurized to 100 psig and the temperature ramped up to 50 °C. After 10 minutes at 50 °C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80 °C resulting in 1.9 g of a white rubbery solid (560,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 30 °C. ^{1}H NMR: 87 branches/1000 carbon atoms. GPC: Mn = 557,000; Mw/Mn = 1.82.

Example 53

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of $(CH_3CH_2)_2AlCl$

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.5 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane. The autoclave was heated to 45 °C and 0.2 mL of $(CH_3CH_2)_2AlCl$ (500 equiv.) in toluene was added. The reactor was rapidly pressurized to 100 psig and the temperature ramped up to 50 °C. After 10 minutes at 50 °C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80 °C resulting in 2 g of a white rubbery solid (590,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 30 °C. ^{1}H NMR: 85 branches/1000 carbon atoms. GPC: Mn = 515,000; Mw/Mn = 1.81.

Example 54

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane in the presence of $(CH_3CH_2)_2AlCl$

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.5 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane. The autoclave was heated to 45 °C and 0.04 mL of $(CH_3CH_2)_2AlCl$ (100 equiv.) in toluene was added. The reactor was rapidly pressurized to 100 psig and the temperature ramped up to 50 °C. After 10 minutes at 50 °C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80 °C resulting in 1.5 g of a white rubbery solid (440,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 29 °C. ^1H NMR: 80 branches/1000 carbon atoms. GPC: Mn = 422,000; Mw/Mn = 1.97.

Example 55

Copolymerization of ethylene and ethyl undecenoate with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MMAO (23 % iso-butylaluminoxane).

A flame dried Schlenk flask equipped with a stir bar and a rubber septum was charged with 50 ml of toluene and 5 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The flask was cooled to 0 °C in an ice-water bath and filled with ethylene (1 atmosphere). To the flask was added 2.0 ml of MMAO in heptane (6.42 wt% aluminum). Within 5 seconds, 5 ml of ethyl undecenoate was added to give a purple solution. The mixture was left to stir for 16 hours. Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the polymer.

The polymer was collected by suction filtration and washed with copious amounts of acetone to ensure all of the ethyl undecenoate comonomer was removed resulting in 100 mg of white powdery polymer. NMR spectroscopic analysis is consistent with the preparation of an ester group containing copolymer. In addition, ethylene homopolymer, which resulted from the short reaction time prior to addition of the ethyl undecenoate, was present. ^{1}H NMR: 7.5 wt % ethyl undecenoate incorporated. GPC: M_n = 9500, M_w/M_n = 16.6. DSC: T_m = 128 °C.

Example 56

Co-polymerization of ethylene and 1,13-tetradecadiene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was flame-dried under vacuum, refilled with ethylene, and then sequentially charged with 50 mL of dry, deoxygenated toluene, 6.0 mL of deoxygenated 1,13-tetradecadiene, and 1.0 mL of a stock solution of 11.8 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in 10.0 mL of dry, deoxygenated dichloromethane. The flask was placed in a 23° C water bath and allowed to equilibrate with 1 atmosphere of ethylene for 5 minutes, then 4.0 mL of a 10 wt% solution of MAO in toluene was added and the mixture was stirred under 1 atmosphere of ethylene. Ethylene uptake was observed and the mixture rapidly became more viscous. After 7 minutes, the reaction was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The co-polymer which separated was isolated by vacuum filtration and dried in vacuo at 100° C for 24 hours to obtain 0.72 g of a rubbery white polymer, which formed a gel upon attempted re-dissolution in hot *o*-dichlorobenzene.

Exampl 57

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 3.4 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The resultant suspension was cooled to 0° C and allowed to equilibrate with 1 atmosphere ethylene for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. A white polyethylene precipitate (with a faint yellow-orange tinge) was observed within minutes. After 38 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene that separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.05-0.1 mm Hg) for 18 hours to give 6.0 g of a white polyethylene (54,000 TO/h). ^1H NMR: 19 branches/1000 carbon atoms. GPC: M_n = 504,000; M_w/M_n = 2.3.

Example 58

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(benzyloxymethyl)-5,6-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MAO.

A 500 mL round bottom flask was fitted with a Schlenk adapter and equipped with a magnetic stir bar and capped with a septum was charged with 100 mL of dry, deoxygenated toluene. The flask was placed in a water bath and allowed to equilibrate with 1 atmosphere ethylene for 19 minutes, then 0.25 mL of a stock solution prepared from 10.0 mg of the nickel dibromide complex of 2,3-bis(benzyloxymethyl)-5,6-bis(2,6-dimethylphenylimino)-[1,4]dioxane and 10.0 mL dichloromethane was added. The reaction mixture was then treated with 4.0 mL of a 10 wt%

solution of MAO in toluene and stirred under 1 atmosphere ethylene. Ethylene uptake and formation of a polyethylene precipitate were observed. After 6.5 minutes, the mixture was quenched by the addition of acetone, methanol and 6 N aqueous HCl. The swollen polyethylene which separated was isolated by vacuum filtration, then dried at 80° C *in vacuo* for several hours. 392 mg of white polyethylene was isolated (404,000TO/h). DSC: (2nd heat) melt with an endothermic maximum at 120 C. ^{1}H NMR: 16 branches/1000 carbon atoms. GPC: M_n = 125,000; M_w/M_n = 2.8.

Example 59

Polymerization of ethylene with the nickel dibromide complex of 5-methoxymethyl-2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 3.8 mg of the nickel dibromide complex of 5-methoxymethyl-2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The resultant suspension was cooled to 0 °C. and allowed to equilibrate with 1 atmosphere ethylene for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. After 10 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.05-0.1 mm Hg) for 48 hours to give 1.04 g of a white, powdery polyethylene. A similar reaction, also at 0° C, was conducted using 0.655 g (equivalent to 0.57 mg of the nickel complex) of a stock solution of 11.6 mg nickel dibromide complex of 5-methoxymethyl-2,3-bis-(2,6-dimethylphenylimino)-[1,4]dioxane in 13.238 g dichloromethane to obtain 291 mg white, powdery polyethylene after 15 minutes reaction.

Example 60

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.3 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane. The autoclave was heated to 60 °C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig and the temperature ramped up to 65 °C. After 10 minutes at 65 °C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80° C. 1.3 g of a white rubbery solid was isolated (480,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 76 °C. ^{1}H NMR: 33 branches/1000 carbon atoms. GPC: Mn = 42,000; Mw/Mn = 1.82.

Example 61

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in example 60 was followed except the polymerization was conducted at 25 °C resulting in 0.59 g of polyethylene (226,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 125 °C. ^{1}H NMR: 9 branches/1000 carbon atoms. GPC: Mn = 237,000; Mw/Mn = 2.15.

Example 62

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in example 60 was followed except the polymerization was conducted at 80 °C resulting in 0.29 g of polyethylene (110,000 TO/h). ^{1}H NMR: 69 branches/1000 carbon atoms. GPC: Mn = 23,000; Mw/Mn = 1.65.

Example 63

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in example 60 was followed except the polymerization was conducted at 50 °C resulting in 3.1 g of polyethylene (1,200,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 95 °C. ^{1}H NMR: 48 branches/1000 carbon atoms. GPC: Mn = 63,000; Mw/Mn = 1.92.

Example 64

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 0.5 mL of a stock solution (10 mg in 10 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane. The autoclave was heated to 60 °C and 2 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig and the temperature ramped up to 65 °C. After 10 minutes at 65 °C, the reaction was quenched by the

addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80 °C. 2.5 g of a white rubbery solid was isolated (660,000 TO/h). DSC: (2nd heat) broad melt with an endothermic maximum at 30 °C. ^{1}H NMR. 82 branches/1000 carbon atoms. GPC: Mn = 147,000; Mw/Mn = 1.91

Example 65

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in example 64 was followed except the polymerization was conducted at 50 °C resulting in 3.4 g of polyethylene (900,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 50 °C. ^{1}H NMR: 65 branches/1000 carbon atoms. GPC: Mn = 219,000; Mw/Mn = 1.85.

Example 66

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in example 64 was followed except the polymerization was conducted at 25 °C resulting in 1.22 g of polyethylene (320,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 112 °C. ^{1}H NMR: 17 branches/1000 carbon atoms. GPC: Mn = 476,000; Mw/Mn = 2.02.

Example 67

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

The procedure described in example 64 was followed except the polymerization was conducted at 80 °C resulting in 0.9 g of polyethylene

(240,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at – 10 °C. ^{1}H NMR: 99 branches/1000 carbon atoms. GPC: Mn = 98,800; Mw/Mn = 1.81.

Example 68

Copolymerization of ethylene and ethyl undecenoate with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane in the presence of MMAO (23 % iso-butylaluminoxane).

A flame dried Schlenk flask equipped with a stir bar and a rubber septum was charged with 50 ml of toluene and 6 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane. The flask was cooled to 0 °C in an ice-water bath and filled with ethylene (1 atmosphere). To the flask was added, 2.0 ml of MMAO in heptane (6.42 wt% aluminum). Within 15 seconds 2.5 ml of ethyl undecenoate was added to give a purple solution. The mixture was left to stir for 16 hours. Acetone, methanol and 6M HCl were added to quench the reaction and precipitate the polymer. The polymer was collected by suction filtration and washed with copious amounts of acetone to ensure all of the ethyl undecenoate comonomer is removed resulting in 510 mg of white powdery polymer. NMR spectroscopic analysis is consistent with the preparation of an ester group containing copolymer. In addition, ethylene homopolymer, which resulted from the short reaction time prior to addition of the ethyl undecenoate, was present. IR: CO stretch at 1742 cm^{-1}. ^{1}H NMR: 1.0 wt % ethyl undecenoate incorporated. GPC: M_n = 61,000, M_w/M_n = 6.4. DSC: T_m = 125 °C.

Example 69

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-4-methylmorpholine in the presence of MAO.

A 1 L Fischer-Porter bottle was assembled onto a pressure head equipped with a mechanical stirrer and gas and liquid feed-through ports, then pressurized to 75 psig of ethylene and relieved to ambient pressure seven

times. The bottle was immersed in a 54° C. water bath, then 100 mL of dry, deoxygenated toluene was added via syringe. The mixture was re-pressurized with ethylene at 75 psig and stirred at 300 rpm for 5 minutes to saturate the solution with ethylene, then the pressure was again relieved, and 4.0 mL of a 10 wt% solution of MAO in toluene was quickly added. The apparatus was again re-pressured to 75 psig ethylene and stirred at 300 rpm for another 5 min to ensure saturation with ethylene. The pressure was once again relieved to ambient pressure and 0.5 mL of a stock solution prepared from 10.0 mg of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-4-methylmorpholine and 10 mL dichloromethane was quickly added and the system quickly pressurized once again with ethylene to 75 psig. After 7 min the pressure was relieved to atmospheric and the reaction was quenched by addition of 5 mL methanol. After the apparatus was disassembled, an additional 50 mL methanol, 50 ml aqueous 6N HCl and 20 mL acetone was added. The resultant organic layer was separated, washed with 6 N aqueous HCl (1 x 25 mL), and water (2 x 50 mL), then concentrated by rotary evaporation under reduced pressure (10 Torr) at 40° C. The residue was then treated with toluene (50 mL) and re-concentrated to afford 134 mg of a very rubbery, clear polyethylene (55,000 TO/h). ^1H NMR: 134 branches/1000 carbon atoms. GPC: M_n = 169,000; M_w/M_n = 1.4.

Example 70

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethyl-phenylimino)-4-methylmorpholine in the presence of MMAO.

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and 1 mL of a stock solution (10 mg in 20 mL CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethyl-phenylimino)-4-methylmorpholine. The autoclave was heated to 45 °C and

3 mL of MMAO in heptane (6.42 wt% aluminum) was added. The reactor was rapidly pressurized to 100 psig and the temperature ramped up to 50 °C After 10 minutes at 50°C, the reaction was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80 °C resulting in 0.87 g of a white rubbery solid was isolated (138,000 TO/h). ^{1}H NMR 97 branches/1000 carbon atoms.

Example 71

Polymerization of ethylene with the nickel dibromide complex of 1,3-bis(4-methoxy-2,6-dimethylphenyl)-4,5-bis(4-methoxy-2,6-dimethylphenylimino)imidazolidin-2-one in the presence of MAO.

A 500 mL round bottom flask fitted with a Schlenk adapter and equipped with a magnetic stir bar and capped with a septum was evacuated, flame-dried, then refilled with ethylene. The flask was provided with a room temperature (ca. 23°C) water bath, then charged with 100 mL of dry, deoxygenated toluene and allowed to equilibrate with 1 atmosphere ethylene for 30 minutes while stirring at 1000 rpm. The reaction mixture was then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene, then 0.10 mL of a stock solution prepared from 6.0 mg of the nickel dibromide complex of 1,3-bis(4-methoxy-2,6-dimethylphenyl)-4,5-bis (4-methoxy-2,6-dimethylphenylimino)imidazolidin-2-one and 6.0 mL dichloromethane was added. After about 7 min and 20 seconds an additional 0.25 mL of the stock solution was added. After 15 more minutes, the reaction mixture was quenched by the addition of acetone, methanol and 6 N aqueous HCl. The polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried on the filter for 2 h, then further dried 13 days in a vacuum oven at 80°C to obtain 172 mg white polyethylene. DSC: (2nd heat) melt with an endothermic maximum at 124°

C. [1]H NMR showed this material to contain approximately 18 branches/1000 carbon atoms. GPC: M_n = 56,500; M_w/M_n = 3.55.

Example 72

Polymerization of ethylene with the reaction product of 1,3-bis-(2,6-dimethyl-phenyl)-4,5-bis-(2,6-dimethyl-phenylimino)-imidazolidin-2-one, (1,2-dimethoxyethane)nickel(II) dibromide, and silver tetrafluoroborate in the presence of MAO.

A 500 mL round bottom flask fitted with a Schlenk adapter, capped with a septum, and equipped with a magnetic stir bar was charged with 100 mL of dry, deoxygenated toluene. The flask was placed in a water bath and allowed to equilibrate with 1 atmosphere ethylene for 10 minutes, then 0.10 mL of a stock solution (freshly prepared from 240 mg of the reaction product of 1,3-bis-(2,6dimethylphenyl)-4,5-bis-(2,6-dimethylphenylimino)-imidazolidin-2-one, (1,2-dimethoxyethane)nickel(II) dibromide, and silver tetrafluoroborate in 10 mL dry, deoxygentated dichloromethane) was added. The reaction mixture was then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. Ethylene uptake and formation of a polyethylene precipitate were observed. After 6.33 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration, then dried at 80° C *in vacuo* for several hours. 860 mg of a white powdery polyethylene was isolated (87,000 TO/h). [1]H NMR: 15 branches/1000 carbon atoms. GPC: M_n = 76,000; M_w/M_n = 2.6

Example 73

Polymerization of ethylene using a catalyst generated in situ from tetrakis(2,6-dimethylphenyl)oxalamidine, bis(1,5-cyclooctadiene)nickel(0) and $HB(Ar)_4$ (Ar = 3,5-bis(trifluoromethyl)phenyl).

A 250 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 8.0 mg of bis(1,5-

cyclooctadiene)nickel(0), 19 mg of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine, and 33 mg of the ether solvate of $HB(Ar)_4$. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The yellow solution which resulted was stirred under ethylene at 0° C for 30 minutes, then warmed to 25° C and stirred for another 30 minutes under ethylene before being quenched by addition of acetone (50 mL), and methanol (50 mL). The polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.5 mm Hg) for 14 hours to give 0.70 g of an elastic white polyethylene (average 860 TO/h). ^{1}H NMR: 83 branches/1000 carbon atoms. GPC: M_n = 173,000; M_w/M_n = 2.8.

Example 74

Polymerization of ethylene with the nickel dibromide complex of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine in the presence of MAO.

A 250 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 10.4 mg of the nickel dibromide complex of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The resultant suspension was cooled to 0° C and allowed to equilibrate with 1 atmosphere ethylene for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene. The yellow solution which resulted was stirred under ethylene at 0° C for 1 hour, and then quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.5 mm Hg) for 14 hours to give 1.3 g of a clear elastic

polyethylene (2531 TO/h). ^{1}H NMR: 91 branches/1000 carbon atoms. GPC: M_n = 127,000; M_w/M_n = 1.3.

Example 75

Ethylene polymerization using complex **XXXV.**

A flame dried Schlenk flask equipped with a stir bar and a rubber septum was charged with 50 ml of methylene chloride and 50 mg of the palladium complex **XXXV**. The flask was placed under an ethylene atmosphere (1 atmosphere). The mixture was left to stir for 20 hours. Acetone and methanol were added to quench the reaction and precipitate the polymer. The polymer was collected and dried *in vacuo* resulting in 2.6 g of tacky polymer. NMR spectroscopic analysis is consistent with the preparation of an ethylene homopolymer. ^{1}H NMR: highly branched polyethylene. GPC: M_n = 34,000, M_w/M_n = 2.5. DSC: T_m = -39 °C, T_g = -69 °C.

Example 76

Propylene polymerization using complex **XXXV.**

A flame dried Schlenk flask equipped with a stir bar and a rubber septum was charged with 50 ml of methylene chloride and 50 mg of the palladium complex **XXXV**. The flask was placed under a propylene atmosphere (1 atmosphere). The mixture was left to stir for 20 hours. Acetone and methanol were added to quench the reaction and precipitate the polymer. The polymer was collected and dried *in vacuo* resulting in 580 mg of tacky polymer. ^{1}H NMR: 192 branch points/1000 carbon atoms. GPC: M_n = 17,000, M_w/M_n = 2.08. DSC: T_g = -53 °C.

Example 77

Ethylene/vinyl ethylene carbonate copolymerization using complex **XXXV.**

A 200 mL flame dried pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with (2,6-di-isopropylphenylimino)-[1,4]dithiane Pd(II) catalyst **XXXV** (100 mg) in an argon filled glove box. Upon removal from the glove box, the flask was

evacuated and backfilled with ethylene. The catalyst was dissolved in CH_2Cl_2 (25 mL) and immediately treated with vinyl ethylene carbonate (5mL). The resulting orange solution was stirred at 23 °C under an ethylene atmosphere (1 atm) for 20 hours. A small amount of polymer had precipitated out of solution. The polymerization was quenched with MeOH and acetone leaving gray oil adhering to the walls of the flask. The polymer was washed several times with acetone and MeOH to remove any remaining monomer. The polymer was dissloved in CH_2Cl_2 and transferred to a storage jar. The solvent was left to evaporate and the resulting oily polymer was dried *in vacuo* at ~80 °C for 3 days to afford a tacky solid (2.15 g, 1100 TO). ^{1}H NMR was consistent with a copolymer containing approximately 96.5 weight % ethylene and 3.5 weight % vinyl ethylene carbonate monomer units.; M_n 40,200 $^g/_{mol}$; M_w 92,100 $^g/_{mol}$; DSC T_g –68 °C, T_m –38 °C.

Example 78

Ethylene/vinyl ethylene carbonate copolymerization using complex **XXXV.** A 200 mL flame dried pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with (2,6-di-isopropylphenylimino)-[1,4]dithiane Pd(II) catalyst **XXXV** (100 mg) in an argon filled glove box. Upon removal from the glove box, the flask was evacuated and backfilled with ethylene. The catalyst was dissolved in CH_2Cl_2 (20 mL) and immediately treated with vinyl ethylene carbonate (10mL). The resulting orange solution was stirred at 23 °C under an ethylene atmosphere (1 atm) for 28 hours. A small amount of polymer had precipitated out of solution. The polymerization was quenched with MeOH and acetone leaving gray oil adhering to the walls of the flask. The polymer was dissloved in CH_2Cl_2 and transferred to a storage jar. The solvent was left to evaporate and the resulting oily polymer was washed several times with acetone and MeOH to remove any remaining monomer and dried *in vacuo* at ~80 °C for 1 day to afford a tacky solid (1.15 g, 613 TO). ^{1}H NMR

was consistent with a copolymer containing approximately 95.5 weight % ethylene and 4.5 weight % vinyl ethylene carbonate monomer units.; M_n 15,400 $^g/_{mol}$; M_w 96,000 $^g/_{mol}$; DSC T_g –64 °C, T_m –31 °C.

Example 79

Preparation of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane.

A Schlenk flask equipped with a magnetic stir bar was charged with 100 mg of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dioxane (0.25 mmol) and 71 mg of (1,2-dimethoxyethane)nickel(II) dibromide (0.23 mmol) under an argon atmosphere. Dry, deoxygenated dichloromethane (15 mL) was added and the mixture was stirred under an argon atmosphere, turning red-brown within about 10 minutes. After 2 hours, the red/orange solution was transferred via filter cannula to a new flame dried Schlenk to remove trace amount of unreacted (1,2-dimethoxyethane)nickel(II) dibromide. The CH_2Cl_2 was removed *in vacuo*. The resulting red-brown solid was washed with 2x10 mL of hexane and the solid was dried *in vacuo* for several hours affording 80 mg of a brown solid.

Example 80

Preparation of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 752 mg of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 200 mg of sodium hydride (60% mineral oil dispersion), 5.0 mL of dry tetrahydrofuran, and 250 mg of 2-mercaptoimidazole. The mixture was heated at reflux for 120 minutes. After cooling, the mixture was diluted with water and dichloromethane, and the organic layer was separated and concentrated to afford a yellow-orange oil. Column chromatography (SiO_2, Merck Grade 9385 230-400 mesh, 60 Å; 12 v% ethyl acetate in hexane) afforded 487 mg

of a yellow-orange solid. Recrystallization from heptane gave 366 mg yellow-orange prisms. Field desorption mass spectrometry showed a parent ion peak at 360 m/z.

Example 81

Preparation of N^1, N^2-bis(2,6-dimethylphenyl)ethanediimidoselenoic acid diphenyl ester.

A 50 mL round bottom flask equipped with a magnetic stir bar and a reflux condenser capped by a nitrogen inlet was charged with 961 mg of N^1,N^2-bis(2,6-dimethylphenyl)oxalodiimidoyl dichloride, 287 mg of sodium hydride (60% mineral oil dispersion), 8.2 mL of dry tetrahydrofuran, and .068 mL of benzeneselenol. The mixture was heated at reflux for 45 minutes. After cooling, the mixture was diluted with water and diethyl ether. The ether layer was separated and washed again with water, then concentrated *in vacuo* to afford a yellow-orange crystalline solid. The solid was dissolved in hot hexane, then filtered, and then reconcentrated. Recrystallization from heptane afforded 745 mg orange prisms, 1st crop. Field desorption mass spectrometry showed a parent ion cluster of peaks from 570-578 m/z. ^{1}H NMR (300 MHz, $CDCl_3$, chemical shifts in ppm relative to TMS at 0 ppm): 1.95 (12 p, s), 6.75 (6p, app s), 7.02-7.20 (6p, m), 7.39-7.48 (4p, m).

Example 82

Polymerization of ethylene using a catalyst generated in situ from N^1, N^2-bis(2,6-dimethylphenyl)ethanediimidoselenoic acid diphenyl ester, bis(1,5-cyclooctadiene)nickel(0) and $HB(Ar)_4$ (Ar = 3,5-bis(trifluoromethyl)phenyl).

A 250 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 5 mg of bis(1,5-cyclooctadiene)nickel(0), 10 mg of N^1, N^2-bis(2,6-dimethylphenyl)ethanediimidoselenoic acid diphenyl ester, and 25 mg of the ether solvate of $HB(Ar)_4$. The flask was evacuated and refilled with ethylene, then charged with 45 mL of dry, deoxygenated toluene. The

yellow solution which resulted was stirred under ethylene at 21° C for 10 minutes, then quenched by addition of methanol (50 mL). The polyethylene which separated was isolated by vacuum filtration and washed with methanol, then dried under reduced pressure (0.5 mm Hg) for 14 hours to give 0.060 g of an elastic blue-green polyethylene. ^{1}H NMR: 24 branches/1000 carbon atoms. GPC: M_n = 181,000; M_w/M_n = 3.5.

Example 83

Preparation of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 141 mg of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole and 110 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) was added and the mixture was stirred under an argon atmosphere. After 1 hour, another 5 mL of dichloromethane was added. The mixture was stirred another 16 hours at 21° C, then diluted with 10 mL of dry, deoxygenated hexane and stirred another 3 hours. The supernatant was removed via a filter paper-tipped cannula, and the residue dried *in vacuo* at 1 mm Hg to afford 66 mg of a brown microcrystalline solid.

Example 84

Polymerization of ethylene with the nickel dibromide complex 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 2.5 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole. The flask was evacuated and refilled with ethylene, then charged with 75 mL of dry, deoxygenated toluene. The resultant suspension allowed to equilibrate with 1 atmosphere ethylene at

21 ^{0}C for 15 minutes, then treated with 200 μL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. After 21 min, the reaction was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.05-0.1 mm Hg) for 24 hours to give 198 mg of a white polyethylene. ^{1}H NMR: 13 branches/1000 carbon atoms. GPC: bimodal, with M_n = 23,000; M_p = 366,000; M_w/M_n = 13.5.

Example 85

Preparation of the nickel dibromide complex of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine.

A 50 mL Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 100 mg of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine and 55 mg of (1,2-dimethoxyethane)nickel(II) dibromide under an inert atmosphere. Dry, deoxygenated dichloromethane (5 mL) was added and the mixture was stirred under an argon atmosphere. After 1 hour, another 5 mL of dichloromethane was added. The mixture was stirred another 16 hours at 21° C, then diluted with 10 mL of dry, deoxygenated hexane and stirred another 3 hours. The supernatant was removed via a filter paper-tipped cannula, and the residue dried *in vacuo* at 1 mm Hg to afford 95 mg of light green crystals.

Example 86

Polymerization of ethylene with the nickel dibromide complex of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 2.4 mg of nickel dibromide complex of N^1,N^2,N^3,N^4-tetrakis(2,6-dimethylphenyl)oxalamidine. The flask was evacuated and refilled with ethylene, then charged with 75

mL of dry, deoxygenated toluene. The resultant suspension allowed to equilibrate with 1 atmosphere ethylene at 21 °C for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. After 30 min, the reaction was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen polyethylene which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (0.05-0.1 mm Hg) for 24 hours to give 743 mg of a white polyethylene. ^{1}H NMR: 112 branches/1000 carbon atoms. GPC: M_n = 330,000; M_w/M_n = 1.4.

Example 87

<u>Copolymerization of ethylene and 1-pentene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.</u>

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 0.5 mL of a stock solution of 12.4 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in 10.0 mL dichloromethane. The flask was evacuated and refilled with ethylene, then charged with 100 mL of dry, deoxygenated toluene, and 5.0 mL 1-pentene. The resultant suspension was cooled to 0 °C and allowed to equilibrate with 1 atmosphere ethylene for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. After 45 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen copolymer which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (255 mm Hg) at 100 °C for 24 hours to obtain 2.0 g of white coploymer. ^{1}H NMR: 24 branches/1000 carbon atoms. ^{13}C NMR: 7.6 methyl branches/1000 carbons, 1.2 ethyl branches/1000 carbons, 9.1 propyl branches/1000

carbons, 2.1 butyl branches/1000 carbons, 3.4 pentyl and higher alkyl branches/1000 carbons. GPC: M_n = 274,000; M_w/M_n = 2.3.

Example 88

Copolymerization of ethylene and 1-heptene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.

A 200 mL pear-shaped Schlenk flask equipped with a magnetic stir bar and capped with a septum was charged with 0.5 mL of a stock solution of 12.4 mg of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in 10.0 mL dichloromethane. The flask was evacuated and refilled with ethylene, then charged with 100 mL of dry, deoxygenated toluene, and 5.0 mL 1-heptene. The resultant suspension was cooled to 0 °C and allowed to equilibrate with 1 atmosphere ethylene for 15 minutes, then treated with 4.0 mL of a 10 wt% solution of MAO in toluene and stirred under 1 atmosphere ethylene. After 33 minutes, the mixture was quenched by the addition of acetone (50 mL), methanol (50 mL) and 6 N aqueous HCl (100 mL). The swollen copolymer which separated was isolated by vacuum filtration and washed with water, methanol and acetone, then dried under reduced pressure (255 mm Hg) at 100 ^{0}C for 24 hours to obtain 1.25 g of white coploymer. ^{1}H NMR: 19 branches/1000 carbon atoms. ^{13}C NMR: 5.9 methyl branches/1000 carbons, less than 1 ethyl branch/1000 carbons, less than 1 propyl branch/1000 carbons, 1.8 butyl branches/1000 carbons, 11.5 pentyl and higher alkyl branches/1000 carbons. GPC: M_n = 223,000; M_w/M_n = 2.3.

Example 89

Polymerization of 1-hexene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of MAO.

A 22 mL vial equipped with a magnetic stir bar and capped by a septum was sequentially charged with 1.8 mg of the nickel dibromide

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 99/12074

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9840374	A	17-09-1998	WO	9847933 A	29-10-1998
			WO	9840420 A	17-09-1998
WO 9748742	A	24-12-1997	AU	3599297 A	07-01-1998
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			EP	0892979 A	27-01-1999
			NO	984715 A	09-10-1998

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 17,18,27-31,49

1. The expression "capable of abstracting Q- or W- to form a weakly coordinating anion" used in the Claims 17 and 49 is ambiguous.

2. Claim 18 is dependent from the unclear Claim 17.

3. The expression "a free flowing polymer" used in Claim 27 is ambiguous as it is not clear when a polymer becomes free flowing in stead of not free flowing.

4. The expression "broad composition distribution" used in Claim 28 is ambiguous.

5. Claim 29 is dependent from the unclear Claim 28.

6.1 The expression "having an improved rate for the co-polymerization ..... CH2=CH(CH2)nJ" used in Claim 30 is unclear as this claim does not indicate with what this copolymerization should be compared.

6.2 The expression A group 8-10 transition metal ..... ,in an olefin polymerization, which comprises combining" is ambiguous as it seems to use terms directed to a process in a product claim.

7.1 Claim 31 is directed to a method. A method claim cannot be dependent from a product clim like Claim 30.

7.2 Claim 31 is dependent from the unclear Claim 30.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/12074

Box I Observations where certain claims were found uns archable (Continuation of it m 1 f first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. [ ] Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. [X] Claims Nos.: 17,18,27-31,49
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210

3. [ ] Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

B x II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. [ ] As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. [ ] As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. [ ] As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. [ ] No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

[ ] The additional search fees were accompanied by the applicant's protest.

[ ] No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/12074

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F10/00 C08F4/70 C08F4/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X P,Y	WO 98 40374 A (EASTMAN CHEM CO) 17 September 1998 (1998-09-17) the whole document ---	19-26, 32-48 1-16
Y	WO 97 48742 A (GRACE W R & CO) 24 December 1997 (1997-12-24) page 2, line 1 -page 2, line 9 ---	1-16
X	EP 0 776 908 A (UNION CARBIDE CHEM PLASTIC) 4 June 1997 (1997-06-04) claim 1; examples 1-54 ---	19-26
X	WO 97 38424 A (DOW CHEMICAL CO ;KALE LAWRENCE T (US); IACCINO TRUDY L (US); BOW K) 16 October 1997 (1997-10-16) page 13, line 17 -page 27, line 27; claim 10 -----	32-48

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 November 1999	19. 11. 99

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Van Golde, L

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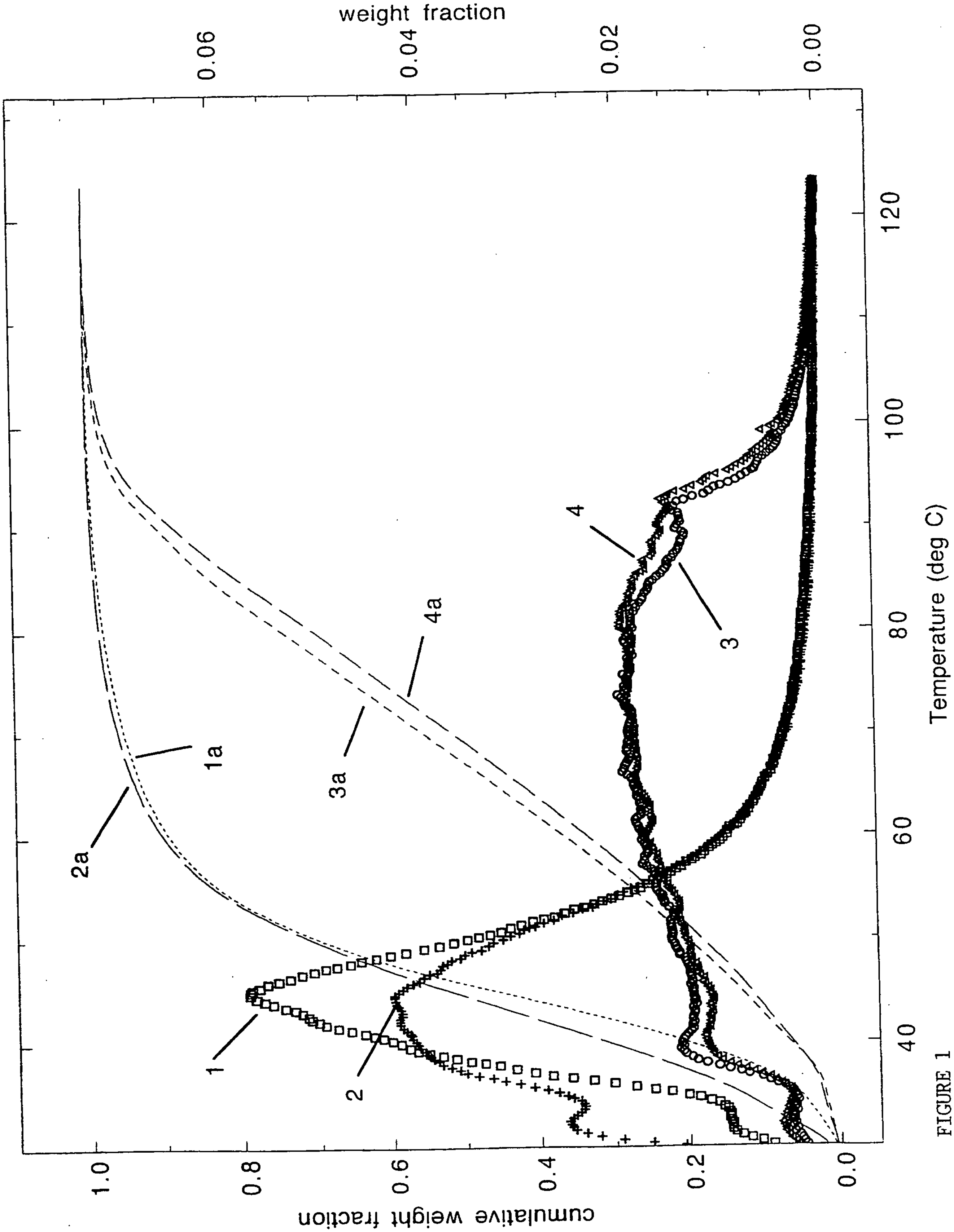
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0.06
0.04
0.02
0.00
cumulative weight fraction
1.0
0.8
0.6
0.4
0.2
0.0
Temperature (deg C)
40
60
80
100
120
1
2
3
4
1a
2a
3a
4a

FIGURE 1

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

47. The polyalkene of claim 45 with a CDBI of less than 30%.

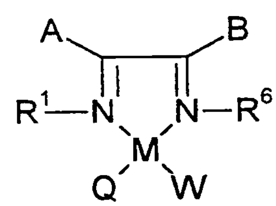
48. The polyalkene as recited in claim 42 which is an ethylene homopolymer.

49. A process for the copolymerization of one or more olefin monomers of the type $RCH{=}CHR^8$ with one or more functional olefin monomers of the formula $CH_2{=}CH(CH_2)_nJ$ comprising a catalyst, in an olefin polymerization reaction which comprises combining a complex of the formula **XII**, a solid support, and optionally a compound Y, prior to the utilization of said catalyst in said olefin polymerization reaction.

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

n is an interger between 1-20;

J is a group selected from ester, acyl, acid halide, aldehyde, alkyl amide, aryl, alkylamine, aryl amine, alkyl amido, aryl amido, alkyl imido, aryl imido, ether, nitrile, alcohol, keto, amino, amido, imido, alkoxy thiol, thioalkoxy, acid, urea, sulfonamido, and sulfoester;



XII

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

contains for every 100 branches that are methyl, about 30 to about 90 ethyl branches, about 4 to about 20 propyl branches, about 15 to about 50 butyl branches, about 3 to about 15 amyl branches, and about 30 to about 140 hexyl or longer branches.

36. The polyalkene of claim 35 with a CDBI of less than 40%.

37. The polyalkene of claim 35 with a CDBI of less than 30%.

38. The polyalkene as recited in claim 35 which contains about 100 to about 130 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 50 to about 75 ethyl branches, about 5 to about 15 propyl branches, about 24 to about 40 butyl branches, about 5 to about 10 amyl branches, and about 65 to about 120 hexyl or longer branches.

39. The polyalkene of claim 38 with a CDBI of less than 40%.

40. The polyalkene of claim 38 with a CDBI of less than 30%.

41. The polyalkene as recited in claim 35 which is an ethylene homopolymer.

42. A polyalkene with a CDBI of less than 50% which contains about 20 to about 150 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 4 to about 20 ethyl branches, 1 to about 12 propyl branches, 1 to about 12 butyl branches, 1 to about 10 amyl branches, and 0 to about 20 hexyl or longer branches.

43. The polyalkene of claim 42 with a CDBI of less than 40%.

44. The polyalkene of claim 42 with a CDBI of less than 30%.

45. The polyalkene as recited in claim 42 which contains about 40 to about 100 branches per 1000 methylene groups, and which contains for every 100 branches that are methyl, about 6 to about 15 ethyl branches, about 2 to about 10 propyl branches, about 2 to about 10 butyl branches, about 2 to about 8 amyl branches, and about 2 to about 15 hexyl or longer branches.

46. The polyalkene of claim 45 with a CDBI of less than 40%.

21. The composition of claim 20, wherein the compound Y is methylaluminoxane.

22. A polyethylene composition comprising a blend of polyethylene polymers, wherein said blend has an average degree of branching of from 5 to 120 alkyl branches per 1000 carbon atoms, wherein any individual component of said blend has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms, wherein said polymers are prepared in one reaction vessel, solely from ethylene, and wherein said polymers are prepared utilizing a Group 8-10 transition metal catalyst which has been reacted with a solid support and optionally a compound Y, in any order, wherein Y is selected from the group consisting of methylaluminoxane and other aluminum sesquioxides having the formulas $R^7{}_3Al$, $R^7{}_2AlCl$, and R^7AlCl_2 ,wherein R^7 is alkyl.

23. The composition of claim 22, wherein the transition metal catalyst is a Ni catalyst.

24. The composition of claim 23, wherein the compound Y is methylaluminoxane.

25. A polyolefin which when fractionated based on solubility using supercritical propane by isothermal increasing profiling and critical, isobaric, temperature rising elution fractionation, into ten fractions between about 40 and about 140 °C, wherein a first fraction taken at about 40 °C has between about 40 and about 100 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 and about 15% are pentyl or longer branches; a second fraction taken between about 40-60 °C has between about 30 and about 90 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 and about

15% are pentyl or longer branches; a third fraction taken between about 60-65 °C has between about 30 and about 80 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 to about 15% are pentyl or longer branches; a fourth fraction taken between about 65-70 °C has between about 20 and about 60 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 1 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 to about 15% are pentyl or longer branches; a fifth fraction taken between about 75-85 °C has between about 10 and about 50 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 to about 15% are pentyl or longer branches; a sixth fraction taken between about 85-95 °C has between about 10 and about 40 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 5 and about 15% are pentyl or longer branches; a seventh fraction taken between about 95-100 °C has between about 5 and about 35 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 and about 15% are pentyl or longer branches; an eighth fraction taken between about 100-110 °C has between about 0 and about 25 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15%

are butyl branches, and between about 0 and about 15% are pentyl or longer branches; a ninth fraction taken between about 110-140 °C has between about 0 and about 30 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 to about 15% are pentyl or longer branches; a tenth fraction taken between about 140-150 °C has between about 0 and about 20 branches per 1000 carbon atoms, wherein between about 50 to about 90% are methyl branches, about 5 to about 15% are ethyl branches, about 0 to about 10% are propyl branches, about 0 to about 15% are butyl branches, and between about 0 to about 15% are pentyl or longer branches; and a tenth fraction has between about 0 and about 20 branches per 1000 carbon atoms.

26. A polymer derived from essentially ethylene alone that has greater than 30 branches per 1000 carbon atoms and a melt transition (endothermic maximum) in the DSC of greater than about 110 °C.

27. The polymer as claimed in claim 26 that is a free flowing polymer.

28. A polymer derived from ethylene alone that has a broad composition distribution and a molecular weight distribution of less than 6 and greater than 2.5, wherein said polymer has an average degree of branching of from 5 to 120 alkyl branches per 1000 carbon atoms, and wherein any individual component of said polymer has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms.

29. The polymer of claim 28 wherein an individual component of the polymer has between about 40 and 100 branches per 1000 carbon atoms, another component has between about 30 and 90 branches per 1000 carbon atoms, another component has between about 30 and 80 branches per 1000 carbon atoms, another component has between about 20 and 60 branches per 1000 carbon atoms, another component has between about

10 and 50 branches per 1000 carbon atoms, another component has between about 10 and 40 branches per 1000 carbon atoms, another component has between about 5 and 35 branches per 1000 carbon atoms, another component has between about 0 and 25 branches per 1000 carbon atoms, another component has between about 0 and 30 branches per 1000 carbon atoms, another component has between about 0 and 20 branches per 1000 carbon atoms.

30. A Group 8-10 transition metal catalyst having an improved rate for the co-polymerization of one or more olefin monomers of the type $RCH=CHR^8$ with one or more functional olefin monomers of the formula $CH_2=CH(CH_2)_nJ$, in an olefin polymerization reaction which comprises combining said catalyst with a solid support, and optionally a Bronsted or Lewis acid in any order, prior to the utilization of said catalyst in said olefin polymerization reaction.

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

n is an interger between 1-20;

J is a group selected from ester, acyl, acid halide, aldehyde, alkyl amide, aryl, alkylamine, aryl amine, alkyl amido, aryl amido, alkyl imido, aryl imido, ether, nitrile, alcohol, keto, amino, amido, imido, alkoxy thiol, thioalkoxy, acid, urea, sulfonamido, and sulfoester.

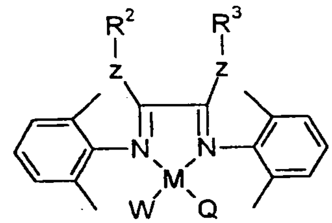
31. The method as described in claim 30 wherein the catalyst is the catalyst of claim 1.

32. A ethylene homopolymer with a CDBI of less than 50 %.

33. The ethylene homopolymer of claim 32 wherein the CDBI is less than 40%.

34. The ethylene homopolymer of claim 32 wherein the CDBI is less than 30%.

35. A polyalkene with a CDBI of less than 50%, which contains about 80 to about 150 branches per 1000 methylene groups, and which



XXIV

wherein R^2 and R^3 are each independently hydrogen, hydrocarbyl, substituted hydrocarbyl, or silyl, or may collectively form a bridging hydrocarbyl, bridging substituted hydrocarbyl, or a substituted silicon atom;

Q is alkyl, chloride, iodide or bromide;

W is alkyl, chloride, iodide or bromide;

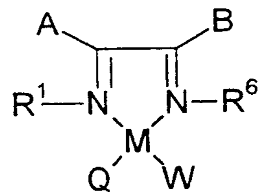
N is nitrogen;

Z is sulfur or oxygen; and

M is Ni(II).

19. A polyethylene composition comprising a blend of polyethylene polymers, wherein said blend has an average degree of branching of from 5 to 120 alkyl branches per 1000 carbon atoms, wherein any individual component of said blend has a degree of branching of from 0 to 150 alkyl branches per 1000 carbon atoms, wherein said polymers are prepared in one reaction vessel, solely from ethylene, and wherein said polymers are prepared utilizing a Group 8-10 transition metal catalyst supported on a solid support which has been pre-treated with a compound Y selected from the group consisting of methylaluminoxane and other aluminum sesquioxides having the formulas $R^7{}_3Al$, $R^7{}_2AlCl$, and R^7AlCl_2 ,wherein R^7 is alkyl.

20. The composition of claim 19, wherein the transition metal catalyst is a Ni catalyst.



XII

wherein R^1 is hydrogen, hydrocarbyl, substituted hydrocarbyl, fluoroalkyl or silyl;

n is an integer greater than 3;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

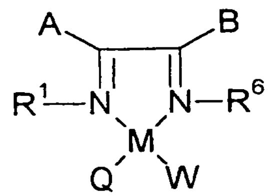
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

18. The process described in claim 17 wherein the compound of formual **XII** is represented by formula **XXIV**.

16. A process for the polymerization of olefins, comprising contacting one or more monomers of the formula $RCH{=}CHR^8$ with a supported catalyst formed by combining a compound of formula **XII**:



XII

with a solid support which has been pre-treated with a compound Y, wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

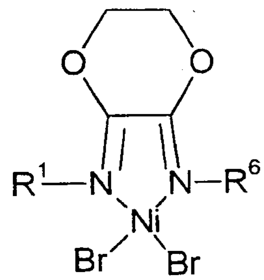
W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

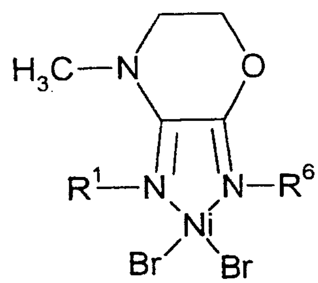
and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

17. A process for the copolymerization of ethylene and a comonomer of the formula $CH_2{=}CH(CH_2)_nCO_2R^1$ which comprises contacting ethylene and a comonomer of the formula $CH_2{=}CH(CH_2)_nCO_2R^1$ with a supported catalyst formed by combining silica with a compound of the formula **XII** and optionally a compound Y;



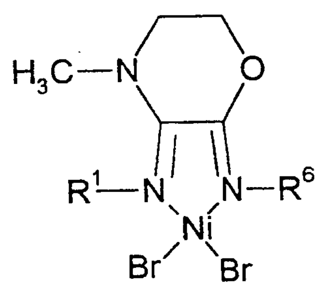
XXXIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;



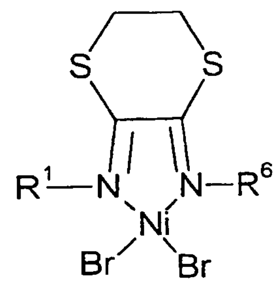
XXXVIII

wherein R^1 and R^6 are 2,6-dimethylphenyl; and



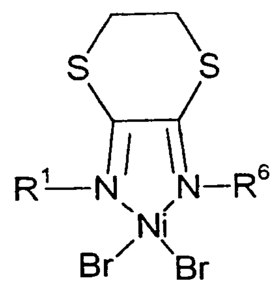
XXXIX

wherein R^1 and R^6 are 2,6-diisopropylphenyl.



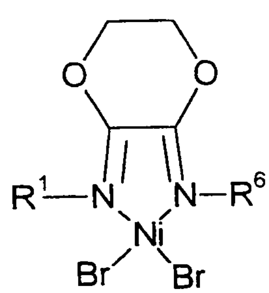
XXVII

wherein R^1 and R^6 are 2,6-dimethylphenyl;



XXVIII

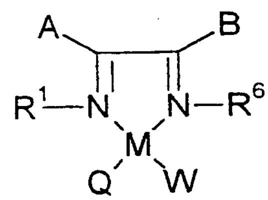
wherein R^1 and R^6 are 2,6-diisopropylphenyl;



XXXII

wherein R^1 and R^6 are 2,6-dimethylphenyl;

13. A process for the polymerization of olefins, comprising contacting one or more monomers of the formula $RCH=CHR^8$ with the reaction product of a compound of formula **XII**, a compound Y and a solid support:



XII

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

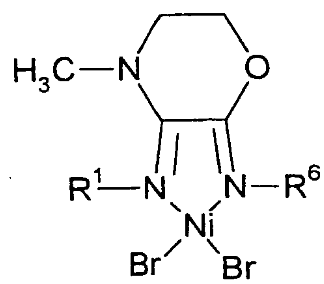
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

14. The process of claim 13 wherein M is Ni(II).

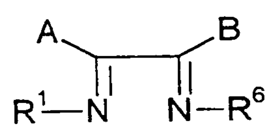
15. The process of Claim 13, wherein the compound of formula **XII** is selected from the group consisting of



XXXIX

wherein R^1 and R^6 are 2,6-diisopropylphenyl.

11. A process for the polymerization of olefins, comprising contacting one or more monomers of the formula $RCH{=}CHR^8$ with a catalyst comprising a group 8-10 transition metal complex of a ligand of the formula **X** and optionally a Bronsted or Lewis acid,



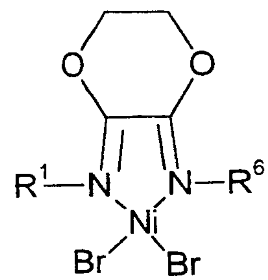
X

wherein R and R^8 each, independently, represent a hydrogen, a hydrocarbyl, or a fluoroalkyl, and may be linked to form a cyclic olefin;

R^1 and R^6 are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

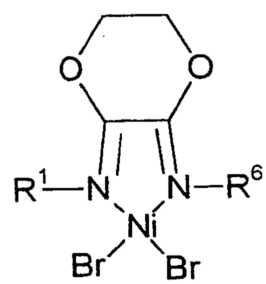
A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the Bronsted or Lewis acid, and the complex are combined in any order.

12. The process of claim 11 wherein the solid support is pretreated with a Bronsted or Lewis acid.



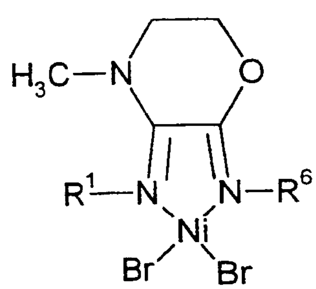
XXXII

wherein R^1 and R^6 are 2,6-dimethylphenyl;



XXXIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;



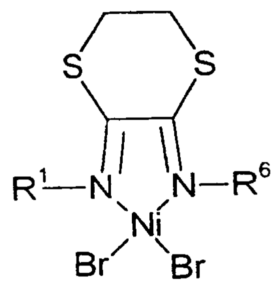
XXXVIII

wherein R^1 and R^6 are 2,6-dimethylphenyl; and

cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

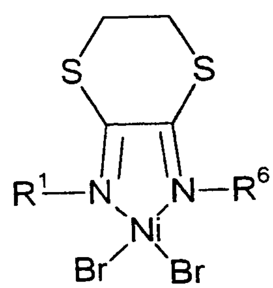
9. The process of claim 8 wherein M is Ni(II).

10. The process of Claim 8, wherein the compound of formula **XII** is selected from the group consisting of



XXVII

wherein R^1 and R^6 are 2,6-dimethylphenyl;



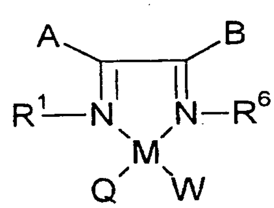
XXVIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the Bronsted or Lewis acid, and the complex are combined in any order to form said supported catalyst.

7. The process of claim 6 wherein the solid support is pretreated with a Bronsted or Lewis acid.

8. A process for the preparation of supported catalysts comprising the reaction product of a compound of formula **XII**, a compound Y and a solid support:



XII

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

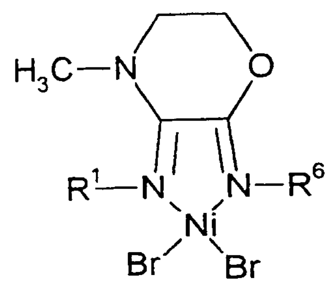
Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

N represents nitrogen; and

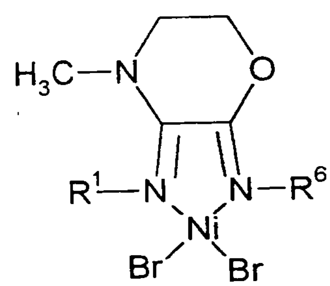
M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a



XXXVIII

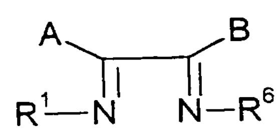
wherein R^1 and R^6 are 2,6-dimethylphenyl; and



XXXIX

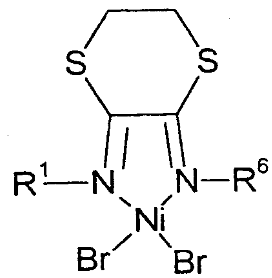
wherein R^1 and R^6 are 2,6-diisopropylphenyl.

6. A process for the preparation of supported catalysts comprising contacting a group 8-10 transition metal complex of a ligand of the formula **X**, a solid support, and optionally a Bronsted or Lewis acid,



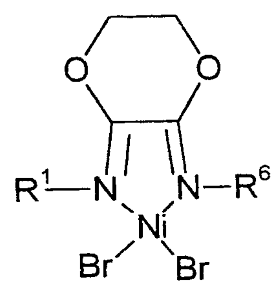
X

wherein R^1 and R^6 are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; **N** represents nitrogen; and



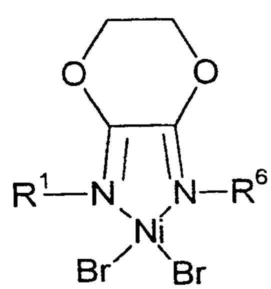
XXVIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;



XXXII

wherein R^1 and R^6 are 2,6-dimethylphenyl;



XXXIII

wherein R^1 and R^6 are 2,6-diisopropylphenyl;

R^1 and R^6 each, independently, represent hydrocarbyl, substituted hydrocarbyl, or silyl;

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group;

Q represents an alkyl, chloride, iodide or bromide;

W represents an alkyl, chloride, iodide or bromide;

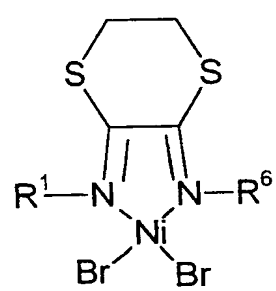
N represents nitrogen; and

M represents Ni(II), Pd(II), Co(II), or Fe(II);

and Y is selected from the group consisting of a neutral Lewis acid capable of abstracting Q^- or W^- to form a weakly coordinating anion, a cationic Lewis acid whose counterion is a weakly coordinating anion, and a Bronsted acid whose conjugate base is a weakly coordinating anion.

4. The catalyst of claim 3 wherein M is Ni(II).

5. The catalyst of Claim 3, wherein the compound of formula **XII** is selected from the group consisting of



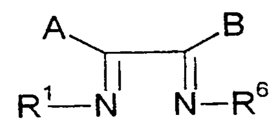
XXVII

wherein R^1 and R^6 are 2,6-dimethylphenyl;

CLAIMS

We claim:

1. A catalyst for the polymerization of olefins comprising a complex comprising (a) a ligand of the formula **X**, (b) a group 8-10 transition metal, and optionally (c) a Bronsted or Lewis acid,



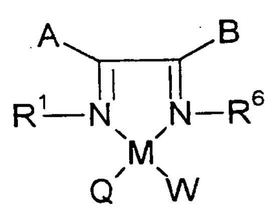
X

R^1 and R^6 are each, independently, hydrocarbyl, substituted hydrocarbyl, or silyl; N represents nitrogen; and

A and B are each, independently, a heteroatom connected mono-radical wherein the connected heteroatom is selected from Group 15 or 16; in addition, A and B may be linked by a bridging group; wherein the complex is attached to a solid support, and wherein the solid support, the Bronsted or Lewis acid, and the complex are combined in any order to form said catalyst.

2. The catalyst of claim 1 wherein the solid support is pretreated with a Bronsted or Lewis acid.

3. A catalyst for the polymerization of olefins comprising the reaction product of a compound of formula **XII**, a compound Y and a solid support:



XII

Example 201

Ethylene Polymerization using the silica supported Ni[η^3-($H_2CC(CO_2Me)CH_2$)] complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A 600 ml Parr® stirred autoclave with 300 g of NaCl (dried in a vacuum oven at 100 °C for 24 hours) and 100 mg of the supported catalyst prepared in example 200 was heated to 50 °C and pressurized rapidly to 400 psig ethylene. The temperature ramped up to 60 °C and the gas phase polymerization was agitated for 1 hour. After 1 hour, the reactor was vented and the contents poured in to a beaker. The polyethylene that resulted was isolated by dissolving the NaCl in a blender and collecting the remaining polymer by filtration. The polyethylene was washed with 6M HCl, water and acetone. The polymer was then dried in a vacuum oven at 100 °C giving 4.7 grams of free flowing polyethylene. DSC: (2nd heat) melt with an endothermic maximum at 122 °C. ^1H NMR: 22 branches/1000 carbon atoms.

A 600 ml Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 200mL of toluene and 2 ml of MAO (10 % weight solution in toluene). The autoclave was heated to 25 °C and pressurized to 100 psig ethylene and 2.0 ml of a stock solution (1 mg in 1 ml toluene) of the Ni[η^3-($H_2CC(CO_2Me)CH_2$)] complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane was added via a high pressure sample loop. The reactor was rapidly pressurized to 400 psig ethylene. After 60 minutes at 25 °C, the reaction was quenched by the addition of methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 80° C. 1.1 g of a powdery white solid was isolated. DSC: (2nd heat) melt with an endothermic maximum at 133 °C. ^{1}H NMR: 2 branches/1000 carbon atoms.

Example 200

<u>Synthesis of the silica supported Ni[η^3-($H_2CC(CO_2Me)CH_2$)] complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.</u>

A flame dried Schlenk flask equipped with a stir bar and a rubber septum was charged with 30mg (22 μmol) Ni[η^3-($H_2CC(CO_2Me)CH_2$)] complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (Witco TA02794/HL/04). The solid mixture was cooled to 0 °C and 20 ml of CH_2Cl_2 was added to the flask and stirred for 45 minutes. After 45 minutes, the solvent was removed in vacuo giving the supported catalyst.

C and pressurized to 500 psig ethylene and 2.0 ml of a stock solution (0.25 mg in 1 ml CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane was added via a high pressure sample loop. The reactor was rapidly pressurized to 600 psig ethylene and the temperature ramped to 80 °C. After 20 minutes at 80 °C, the reaction was quenched by the addition of methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 80° C. 3.0 g of a white rubbery solid was isolated (368,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 77 °C. ^{1}H NMR: 45 branches/1000 carbon atoms. GPC: Mn = 52,300; Mw/Mn = 2.18.

Example 198

Synthesis of the Ni[η^3-($H_2CC(CO_2Me)CH_2$)] complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A flame dried Schlenk flask equipped with a stir bar and a rubber septum was charged with 75 mg [η^3-($H_2CC(CO_2Me)CH_2$) Ni (μ-Br)]$_2$ (0.159 mmol), 293 mg (0.318mmol) sodium tetra[3,5-(trifluoromethylphenyl)] borate and 113 mg (0.318 mmol)of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane. The solid mixture was dissolved in 10 ml of Et_2O. The solution was stirred for 3 hours at room temperature while under an argon atmosphere. After 2 hours, the reaction mixture was filtered and the solvent removed *in vacuo* giving the desired product (328 mg, 75 % yield). [η^3-($H_2CC(CO_2Me)CH_2$) Ni (μ-Br)]$_2$ was synthesized according to the procedure described in Wilke, G. et. al. *Angew. Chem., Int. ed. Engl.* **1966**, *5*, 151.

Example 199

Ethylene Polymerization using the Ni[η^3-($H_2CC(CO_2Me)CH_2$)] complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

vented and the catalyst quenched with methanol and 6 M HCl. The mixture was filtered and the collected solid dried in vacuo at 100 °C to give 1.41 g polymer. M_n = 347.0, M_w = 1077.0, M_w/M_n = 3.1; 5 branches/1000 C (by ^1H NMR); T_m = 134 °C.

Example 196

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of Et_2AlCl.

A 600-ml Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 ml of mineral spirits and 1 ml of Et_2AlCl. The autoclave was heated to 80 °C and 2.0 ml of a stock solution (0.25 mg in 1 ml CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane was added via a high-pressure sample loop. The reactor was rapidly pressurized to 600 psig ethylene. After 20 minutes at 80 °C, the reaction was quenched by the addition of methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 80° C. 3.3 g of a white rubbery solid was isolated (405,000 TO/h). DSC: (2nd heat) melt with an endothermic maximum at 51 °C. ^1H NMR: 45 branches/1000 carbon atoms. GPC: Mn = 60,900; Mw/Mn = 1.90.

Example 197

Polymerization of ethylene with the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane in the presence of Et_2AlCl.

A 600 ml Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 ml of toluene and 2 ml of Et_2AlCl. The autoclave was heated to 75

nitrogen inert atmosphere. The solid readily turned purple. The solid was dried in vacuo at 0 °C and stored at –30 °C. Yield: 615 mg. Calculated Loading of Ni complex/g support: 23 μmol/g.

Example 193

Polymerization of ethylene using **XXVII**^{IW}/MAO^{IW}/2402

A 1000-mL Parr® stirred reactor was charged with 75.2 mg **XXVII**^{IW}/MAO^{IW}/2402 (5 μmol Ni/g; 0.38 μmol Ni) under a nitrogen inert atmosphere. Toluene (300 mL) was added and the reactor pressurized with ethylene (300 psig). The mixture was stirred at 30 °C for 60 min. The vessel was vented and the catalyst quenched with methanol and 6 M HCl. The mixture was filtered and the collected solid dried in vacuo at 100 °C to give 470.3 mg polymer. M_n = 268.1K, M_w = 832.1K, M_w/M_n = 3.1; 3 branches/1000 C (by ^1H NMR); T_m = 132 °C.

Example 194

Treatment of **XXVII**^{IW}/MAO^{IW}/2402 with 1-Hexene by incipient wetness, Hexene^{IW}/**XXVII**^{IW}/MAO^{IW}/2402.

A 20-mL scintillation vial, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with **XXVII**^{IW}/MAO^{IW}/2402 (410.6 mg) and cooled to –30 °C. 1-Hexene (0.5 mL) was then added dropwise with vigorous agitation. A fraction of the resulting solid was stored at –30 °C and another at room temperature.

Example 195

Polymerization of ethylene using Hexene^{IW}/**XXVII**^{IW}/MAO^{IW}/2402

Under a nitrogen inert atmosphere, a 1000-mL Parr® stirred reactor was charged with 55.3 mg Hexene^{IW}/**XXVII**^{IW}/MAO^{IW}/2402 (12 μmol Ni/g; 0.66 μmol Ni) that had been stored at room temperature for 28 days. Toluene (300 mL) was added and the reactor pressurized with ethylene (300 psig). The mixture was stirred at 30 °C for 55 min. The vessel was

inert atmosphere. The flask was evacuated and backfilled with 1 atm ethylene. The suspension was stirred for 2.5 hours before it was quenched with methanol and 6 M HCl. The mixture was filtered and the collected solid dried at 100 °C to give 304 mg. M_n = 59.9K, M_w = 487.3K, M_w/M_n = 8.1; T_m = 125 °C (by DSC).

Example 191

Preparation of MAO supported on silica (Grace Davison XPO-2402) using incipient wetness, $MAO^{IW}/2402$.

A 50-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with silica (Grace Davison XPO-2402; 3.33 g) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. While agitating the content of the flask, 4 mL of MAO (Aldrich, 10 wt% in toluene) was added dropwise. The flask was then placed in vacuo for 2 h, then stored at room temperature under nitrogen for two days. The flask was then heated to 80 °C for 1 h and evacuated. MAO was further added in 4 mL fractions until a total of 24 mL of MAO had been added. Volatiles were removed at room temperature under vacuum between each addition. After additions were complete, the solid was further dried in vacuo for 90 min, yielding 4.80 g solid.

Example 192

Preparation of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on $MAO^{IW}/2402$ by incipient wetness impregnation, **$XXVII^{IW}$**$/MAO^{IW}/2402$.

A 50-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with $MAO^{IW}/2402$ (784.9 mg) and cooled to 0 °C. A solution of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane in dichloromethane (10.4 mg in 1.2 mL) was then added dropwise under a

272.1K, M_w/M_n = 2.0; 52 branches/1000 C (by ^{1}H NMR); T_m = 57 °C (by DSC).

Example 188

Polymerization of ethylene using **XXVII**/DEAC/2212

A 200-mL pear-shaped flask was charged with 81.2 mg **XXVII**/DEAC/2212 (42 μmol Ni/g; 3.4 μmol) under a nitrogen inert atmosphere. The inert atmosphere was replaced by 1 atm ethylene and toluene (50 mL) was added, followed by 2.0 mL DEAC (1.8 M in toluene). The suspension was stirred for 6 min at room temperature. Temperature was controlled with a water bath. The reaction was then quenched with acetone and 6M HCl. The mixture was filtered. The resulting solid was collected and dried in vacuo at 100 °C to give 857 mg. M_n = 179.2K, M_w = 444.7K, M_w/M_n =2.5; 32 branches/1000 C (by ^{1}H NMR); T_m = 110 °C (by DSC).

Example189

Polymerization of ethylene using TMAL/**XXVII**/DEAC/2212

A suspension of TMAL/**XXVII**/DEAC/2212 (3.4 μmol Ni) in toluene (50 mL) was then prepared at 0 °C. The reaction flask was evacuated and backfilled with 1 atm ethylene. The mixture was stirred at room temperature for 2 hours and then quenched with methanol and 6M HCl. The mixture was filtered. The resulting solid was collected and dried in vacuo at 100 °C to give 212 mg. M_n = 215.9K, M_w = 910.6K, M_w/M_n = 4.2; 15 branches/1000 C (by ^{1}H NMR); T_m = 117 °C (by DSC).

Example 190

Polymerization of ethylene using MAO/**XXVII**/DEAC/2212

A 200-mL pear-shaped flask was charged with MAO/**XXVII**/DEAC/2212 (2.9 μmol) and toluene (50 mL) under a nitrogen

A 200-mL pear-shaped flask was charged with 82 mg **XXVII**/DEAC/2402 (40 μmol Ni/g; 3.3 μmol) under a nitrogen inert atmosphere. Toluene (30 mL) was added. The inert atmosphere was then replaced by 1 atm ethylene. The suspension was stirred for 2 hours at room temperature. The reaction was then quenched with acetone and 6M HCl. The mixture was filtered. The resulting solid was collected and dried in vacuo at 100 °C to give 418 mg. M_n = 114.0K, M_w = 264.7K, M_w/M_n = 2.3; 65 branches/1000 C (by ^{1}H NMR); T_m = 110 °C (by DSC).

Example 186

Polymerization of ethylene using **XXVII**/DEAC/2402

A 600-mL Parr® stirred reactor was charged with 80.2 mg (40 μmol Ni/g; 3.2 μmol Ni) under a nitrogen inert atmosphere. Toluene (150 mL) was added and the reactor pressurized with ethylene (800 psig). The mixture was stirred at 40 °C for 58 min. The vessel was vented and the catalyst quenched with methanol and 6 M HCl The mixture was filtered and the collected solid dried in vacuo at 100 °C to give 0.56 g polymer. M_n= 246.5K, M_w = 524.4K, M_w/M_n = 2.1; 9 branches/1000 C (by ^{1}H NMR); T_m = 127 °C (by DSC).

Example 187

Polymerization of ethylene using **XXVII**/DEAC/2212

A 200-mL pear-shaped flask was charged with 89.1 mg **XXVII**/DEAC/2212 (42 μmol Ni/g; 3.7 μmol) under a nitrogen inert atmosphere. The inert atmosphere was replaced by 1 atm ethylene and toluene (50 mL) was added, followed by 2.0 mL MAO (10 wt % in toluene). The suspension was stirred for 10 min at room temperature. Temperature was controlled with a water bath. The reaction was then quenched with acetone and 6M HCl. The mixture was filtered. The resulting solid was collected and dried in vacuo at 100 °C to give 1.80 g. M_n = 132.8K, M_w =

g polymer. M_n= 55.7K, M_w = 651.5K, M_w/M_n = 11.7; 32 branches/1000 C (by ^{1}H NMR); T_m = 113 °C (by DSC).

Example 183

Polymerization of ethylene using **XXVII/MAO/2402**

A 200-mL pear-shaped flask was charged with 57.5 mg **XXVII/MAO/2402** (38 μmol Ni/g; 2.2 μmol) and 645 mg of MAO-treated silica (purchased from Witco TA 02794/HL/04). The nitrogen inert atmosphere was replaced by 1 atm ethylene, and 50 mL anhydrous toluene was then added. The suspension was stirred for 1 hour at room temperature before being quenched with acetone and 6M HCl. The mixture was filtered and the collected solid dried in vacuo at 100 °C to give 478 mg. M_n = 195.5K, M_w = 840.5K, M_w/M_n = 4.3; 16 branches/1000 C; T_m = 116 °C (by DSC).

Example 184

Polymerization of ethylene using **XXVII/MAO/2402**

A 600-mL Parr® stirred reactor was charged with 65.0 mg **XXVII/MAO/2402** (38 μmol Ni/g; 2.5 μmol Ni), 170 mg solid MAO and 214 g sodium chloride under a nitrogen inert atmosphere. The reactor was heated to 60 °C, and subsequently pressurized with 100 psig ethylene. The mixture was further heated to 65 °C and stirred for an additional 45 min. The vessel was vented and the solid mixed with water. The mixture was filtered and the solid washed with water, 6M HCl and methanol. The collected polymer was dried in vacuo at 100 °C to give 2.38 g polymer. M_n= 65.7K, M_w = 487.0K, M_w/M_n = 7.4; 29 branches/1000 C (by ^{1}H NMR); T_m = 118 °C (by DSC).

Example 185

Polymerization of ethylene using **XXVII/DEAC/2402**

A 1000-mL Parr® stirred reactor was charged with 169.3mg (38 μmol Ni/g; 6.4 μmol Ni) under a nitrogen inert atmosphere. Toluene (250 mL) was added and the reactor pressurized with ethylene (800 psig). The mixture was stirred at 40 °C for 60 min. The vessel was vented and the catalyst quenched with methanol and 6 M HCl The mixture was filtered and the collected solid dried in vacuo at 100 °C to give 18.60 g polymer.

Example 181

Polymerization of ethylene using **XXVII/MAO/2402**

A 200-mL pear-shaped flask was charged with 79.3 mg **XXVII**/MAO/2402 (38 μmol Ni/g; 3.0 μmol) under a nitrogen inert atmosphere. The inert atmosphere was replaced by 1 atm ethylene and toluene (50 mL) was added, followed by 2.0 mL MAO (10 wt % in toluene). The suspension was stirred for 11 min at room temperature and then quenched with methanol and 6M HCl. The mixture was filtered. The resulting solid was collected and dried in vacuo at 100 °C to give 643 mg. M_n = 100.5K, M_w = 325.3K, M_w/M_n = 3.2; 41 branches/1000 C (by ^1H NMR); T_m = 83 °C (by DSC).

Example 182

Polymerization of ethylene using **XXVII/MAO/2402**

A 600-mL Parr® stirred reactor was charged with 72.1 mg **XXVII**/MAO/2402 (38 μmol Ni/g; 2.7 μmol Ni) under a nitrogen inert atmosphere. The reactor was then charged with 150 mL anhydrous toluene and heated to 50 °C. I then added 2.0 mL of a 10 wt % solution of MAO in toluene. The vessel was pressurized with 100 psig ethylene and further heated to 69 °C. The slurry agitated for 45 min. The mixture was quenched at elevated pressure by addition of methanol through an injection loop. The vessel was depressurized and the mixture treated with 6M HCl. The polymer was isolated by filtration and dried in vacuo at 100 °C to give 4.21

Example 178

Treatment of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on DEAC/2212 with MAO, MAO/**XXVII**/DEAC/2212.

A 50-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on DEAC/2212, **XXVII**/DEAC/2212 (113.6 mg; 4.8 μmol Ni) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. The solid was cooled to 0 °C and toluene (25 mL) was added under vigorous stirring. After 2 min, the suspension was transferred via canula onto a filter funnel. The resulting solid was dried in vacuo (89 mg) and used to evaluate activity towards ethylene polymerization.

Example 179

Polymerization of ethylene using **XXVII**/MAO/2402

A 50-mL pear-shaped flask was charged with 152.5 mg **XXVII**/MAO/2402 (38 μmol Ni/g; 5.8 μmol) under a nitrogen inert atmosphere. The inert atmosphere was replaced by 1 atm ethylene and toluene (25 mL) was added. The suspension was stirred for 2 hours at room temperature. The reaction was then quenched with acetone and 6M HCl. The mixture was filtered. The resulting solid was collected and dried in vacuo at 100 °C to give 626.5 mg (where 152.5 mg of XXVII/MAO/2402 was used): M_n = 95.5K, M_w = 467.7K, M_w/M_n = 4.9; 27 branches/1000 C (by ^1H NMR); T_m = 118 °C.

Example 180

Polymerization of ethylene using **XXVII**/MAO/2402

Example 176

Preparation of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on DEAC/2212, **XXVII**/DEAC/2212.

A 100-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with DEAC/2212 (758 mg) and the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane (22.1 mg; 38.4 μmol) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. The solid was cooled to 0 °C and dichloromethane (25 mL) was added under vigorous stirring. After 1 hour, the mixture was filtered by canula. The residual solid was then rinsed with 10 mL dichloromethane and filtered by canula a second time. The solid was dried in vacuo and stored at –30 °C. Yield: 718 mg. Loading of Ni complex/g support: 49 μmol (based on Ni analysis) and 34 μmol (based on S analysis). Ni complex:Al ratio: 20 (based on Ni analysis) and 28 (based on S analysis).

Example 177

Treatment of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on DEAC/2212 with trimethylaluminum (TMAL), TMAL/**XXVII**/DEAC/2212.

A 200-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on DEAC/2212, **XXVII**/DEAC/2212 (81.5 mg; 3.4 μmol Ni) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. The solid was cooled to 0 °C and toluene (25 mL) was added under vigorous stirring. After 15 min, the volatile materials were removed in vacuo at 0 °C. The resulting solid was further used to evaluate activity towards ethylene polymerization.

Example 174

Preparation of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on MAO/2402, **XXVII**/MAO/2402.

A 50-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with MAO/2402 (1.62 mg) and the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane (46.7 mg; 81.2 μmol) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. The solid was cooled to 0 °C and dichloromethane (20 mL) was added under vigorous stirring. The volatiles were removed in vacuum. The residual solid was dried in vacuo to give 1.40 g.

Example 175

Preparation of the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane supported on DEAC/2402, **XXVII**/DEAC/2402.

A 50-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with DEAC/2402 (637 mg) and the nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane (18.0 mg; 31.3 μmol) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. The solid was cooled to 0 °C and dichloromethane (25 mL) was added under vigorous stirring. After 1 hour, the mixture was filtered by canula. The residual solid was then rinsed with 10 mL dichloromethane and filtered by canula a second time. The solid was dried in vacuo and stored at –30 °C. Yield: 213.4 mg. Loading of Ni complex/g support: 43 μmol (based on Ni analysis) and 37 μmol (based on S analysis). Ni complex:Al ratio: 22 (based on Ni analysis) and 26 (based on S analysis).

transferred via canula onto a filter funnel. The solid was washed with toluene (1 x 50 mL + 4 x 25 mL) and dried in vacuo to give 6.34 g solid.

Example 172

Preparation of DEAC supported on silica (Grace Davison Sylopol 2212), DEAC/2212.

A 500-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with silica (Grace Davison Sylopol 2212; 3.08 g) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. Upon stirring, anhydrous toluene (80 mL) was then added, followed by 16 mL of a 10 wt % solution of MAO in toluene. The suspension was heated to 80 °C for 4 hours, cooled to room temperature and then transferred via canula onto a filter funnel. The solid was washed with toluene (1 x 50 mL + 6 x 25 mL + 1 x 50 mL) and dried in vacuo to give 3.35 g solid. Obsd wt % Al: 2.6.

Example 173

Preparation of MAO supported on silica (Grace Davison Sylopol 2212), MAO/2212.

A 500-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with silica (Grace Davison Sylopol 2212; 6.27 g) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. Upon stirring, anhydrous toluene (50 mL) was then added, followed by 54 mL of a 10 wt % solution of MAO in toluene. The suspension was heated to 80 °C for 5 hours, cooled to room temperature and then transferred via canula onto a filter funnel. The solid was washed with toluene (1 x 50 mL + 4 x 25 mL) and dried in vacuo to give 6.88 g solid.

transferred via canula onto a filter funnel. The solid was washed with toluene (3 x 50 mL) and dried in vacuo to give 3.64 g solid. BET surface area: 300.9 $m^2\ g^{-1}$. Pore volume: 1.19 $cm^3\ g^{-1}$. Average Pore Diameter: 157.3 Å. Obsd wt % Al: 6.8.

Example 170

Preparation of diethylaluminum chloride (DEAC) supported on silica (Grace Davison XPO-2402), DEAC/2402.

A 500-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with silica (Grace Davison XPO-2402; 3.87 g) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. Upon stirring, anhydrous toluene (80 mL) was then added, followed by 20.0 mL of a 1.8 M of DEAC in toluene. The suspension was heated to 80 °C for 4 hours, cooled to room temperature and then transferred via canula onto a filter funnel. The solid was washed with toluene (5 x 50 mL) and dried in vacuo to give 4.21 g solid. BET surface area: 280 $m^2\ g^{-1}$. Pore volume: 1.0 $cm^3\ g^{-1}$. Average Pore Diameter: 132 Å. Obsd wt % Al: 2.7.

Example 171

Preparation of triethylaluminum (TEAL) supported on silica (Grace Davison XPO-2402), TEAL/2402.

A 500-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with silica (Grace Davison XPO-2402; 6.15 g) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. Upon stirring, anhydrous toluene (50 mL) was then added, followed by 100 mL of a 1.9 mL of TEAL in toluene. The suspension was heated to 80 °C for 4 hours, cooled to room temperature and then

Solution Phase Polymerization

Ex.	Catalyst	Procedure	Mass Polymer (g)	Total TO	M_n	PDI	Branches/ 1000C (^{1}HNMR)	T_m (° C)
160	**XXVII**	A	6	247K	83K	2.42	33	94
161	**XXVII**	B	9	370K	135K	2.61	26	113
162	**XXVII**	C	6	245K	144K	2.30	24	113
163	**XXVII**	D	5.7	116K	66K	1.85	47	80
164	**XXVII**	E	6.3	129K	58K	2.18	44	75
165	**XXVII**	F	7.8	159K	63K	2.43	37	95
166	**XXVII**	G	3.8	78K	52K	1.85	-	55
167	**XXVII**	H	5.5	112K	78K	1.93	45	78
168	**XXVII**	I	1.5	31K	32K	1.85	63	55

Example 169

Preparation of MAO supported on silica (Grace Davison XPO-2402), MAO/2402.

A 500-mL pear-shaped flask, previously heated to 200 °C for several hours and allowed to cool to room temperature under vacuum, was charged with silica (Grace Davison XPO-2402; 3.08 g) under a nitrogen inert atmosphere. The flask was equipped with a magnetic stirring bar and a septum cap. Upon stirring, anhydrous toluene (80 mL) was then added, followed by 19.0 mL of a 10 wt % of MAO in toluene. The suspension was heated to 80 °C for 4 hours, cooled to room temperature and then

C- cocatalyst = Et_2AlCl; mol cat.= 8.7 x 10^{-7}; solvent = mineral spirits; temperature = 65 °C; ethylene pressure = 800 psig; reaction time = 20min.

D- cocatalyst = Et_2AlCl; mol cat.= 17.5 x 10^{-7}; solvent = toluene; temperature = 80 °C; ethylene pressure = 600 psig; reaction time = 20min.

E- cocatalyst = Et_2AlCl; mol cat.= 17.5 x 10^{-7}; solvent = toluene; temperature = 75 °C; ethylene pressure = 600 psig; reaction time = 20min.

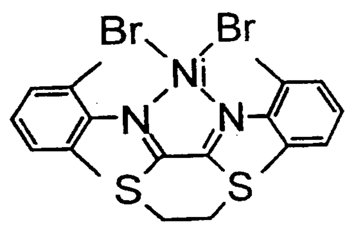
F- cocatalyst = Et_2AlCl; mol cat.= 17.5 x 10^{-7}; solvent = toluene; temperature = 75 °C; ethylene pressure = 800 psig; reaction time = 20min.

G- cocatalyst = Et_2AlCl; mol cat.= 17.5 x 10^{-7}; solvent = toluene; temperature = 80 °C; ethylene pressure = 400 psig; reaction time = 20min.

H- cocatalyst = Et_2AlCl; mol cat.= 17.5 x 10^{-7}; solvent = toluene; temperature = 65 °C; ethylene pressure = 400 psig; reaction time = 20min.

I- cocatalyst = Et_2AlCl; mol cat.= 17.5 x 10^{-7}; solvent = toluene; temperature = 100 °C; ethylene pressure = 800 psig; reaction time = 20min.

Solution Phase Polymerization



XXVII

Solution Phase Polymerization Procedure

A 600 mL Parr ® autoclave was first heated to about 100 °C under high vacuum to ensure the reactor was dry. The reactor was cooled and purged with argon. Under an argon atmosphere, the autoclave was charged with 150 mL of toluene and a stock solution (CH_2Cl_2) of the nickel dibromide complex of 2,3-bis(2,6-dimethyl-phenylimino)[1,4]-dithiane. The autoclave was heated to the desired temperature and a cocatalyst was added. The reactor was rapidly pressurized to the desired pressure. After the desired reaction time, the polymerization was quenched by the addition of acetone, and methanol. The swollen polyethylene which separated was isolated by filtration and dried for several hours in a vacuum oven at 80 °C. As used herein, Et_2AlCl refers to diethyl aluminum chloride.

A- cocatalyst = Et_2AlCl; mol cat.= 8.7×10^{-7}; solvent = mineral spirits; temperature = 80 °C; ethylene pressure = 600 psig; reaction time = 20min.

B- cocatalyst = Et_2AlCl; mol cat.= 8.7×10^{-7}; solvent = mineral spirits; temperature = 65 °C; ethylene pressure = 600 psig; reaction time = 20min.

2015-2030, 1997, and publicly available literature from Phasex Corporation, 360 Merrimack St., Lawrence, MA 01843, and at www.Phasex.com):

Fraction	Temperature Collected (°C)	Weight of Fraction (g)	M_n	PDI	Branching (^{1}H NMR)	T_m (°C)
1	40	0.38	20,500	3.12	71	64
2	40-65	0.60	30,200	3.10	57	70
3	65-75	0.73	43,600	2.73	47	87
4	75-85	0.82	49,900	3.16	35	98
5	85-90	0.54	63,200	2.58	30	106
6	90-95	0.62	81,200	2.42	25	109
7	95-100	0.60	79,700	2.51	22	114
8	100-105	0.89	77,900	3.04	18	118
9	105-110	0.81	117,600	2.30	16	121
10	110-115	0.65	115,000	2.59	13	124
11	115-120	0.39	116,500	2.61	11	126
12	120-125	0.16	139,500	2.43	11	125
13	125-150	0.25	151,300	2.43	-	123
residue	-	2.2	141,000	5.29	-	-
Bulk Sample	-	12	90,700	3.79	30	119

of Poly(ethylene-co-vinyl acetate) in Supercritical Propylene: Towards a Molecular Understanding of a Complex Macromolecule", J. Appl. Polym. Sci., **64**, 2015-2030, 1997, and publicly available literature from Phasex Corporation, 360 Merrimack St., Lawrence, MA 01843, and at www.Phasex.com):

Fraction	Temperature Collected (°C)	Weight of Fraction (g)	M_n	PDI	Branching (^{1}H NMR)	T_m (°C)
1	40	1.43	29,500	2.76	72.2	50
2	40-60	0.43	28,600	3.02	62.3	55
3	60-65	0.74	49,400	2.37	57.5	79
4	65-75	0.52	83,100	2.14	45.9	92
5	75-85	0.80	80,900	2.22	36.5	99
6	85-95	0.50	77,400	2.40	34.3	102
7	95-100	0.61	93,200	2.26	26.3	108
8	100-110	0.47	116,000	2.15	19.3	117
9	110-140	0.41	125,000	2.23	16.7	122
10	140-150	0.15	184,000	2.96	14.3	124
residue	-	3.85	-	-	<5	-
Bulk Sample	-	-	59,900	4.42	48	114

The polymer made in the gas phase in example 138 (12 grams) was fractionated using supercritical propane by isothermal increasing pressure profiling and critical, isobaric, temperature rising elution fractionation to give the following data. (See, B. Folie, et al., "Fractionation of Poly(ethylene-co-vinyl acetate) in Supercritical Propylene: Towards a Molecular Understanding of a Complex Macromolecule", J. Appl. Polym. Sci., **64**,

Gas Phase Polymerization (Part 2)

Ex.	Catalyst	Procedure	Mass Polymer (g)	Total TO	M_n	PDI	Branches/ 1000C (^{1}HNMR)	T_m
139	B	M	7	48K	57K	4.61	43	115
140	C	M	7	48K	79K	3.77	48	116
141	B	H	13.8	94K	106K	3.84	24	120
142	B	H	12.7	87K	99K	3.63	26	120
143	D	J	4	54K	69K	5.53	35	112
144	D	K	3	41K	45K	4.11	56	112
145	D	L	5	68K	117K	3.48	28	115
146	D	M	3.6	50K	70K	3.74	37	115
147	D	H	5	68K	107K	3.24	18	118
148	D	N	5.9	80K	76K	4.2	25	116
149	E	J	3.8	129K	65K	4.86	36	113
150	E	K	1.5	51K	43K	4.4	47	114
151	E	L	4	137K	74K	4.6	28	119
152	F	H	4.7	161K	106K	3.77	14	120
153	G	H	0.35	12K	81K	4.32	23	119
154	G	H	0.25	9K	57K	5.64	27	118
155	F	H	3.8	130K	94K	3.46	18	120
156	A	O	1.8	123K	71K	4.70	29	117
157	A	P	2.1	145K	80K	4.09	33	117
158	A	L	2.3	157K	78K	4.72	30	117
159	B	O	4.9	34K	58K	4.50	38	117

The polymer made in the gas phase in example 131 (10.57 grams) was fractionated using supercritical propane by isothermal increasing pressure profiling and critical, isobaric, temperature rising elution fractionation to give the following data. (See, B. Folie, et al., "Fractionation

N- 100 °C/400 psig ethylene/ 60 min reaction time/ 100 mg of supported catalyst.

O- 80 °C/200 psig ethylene/ 15 min reaction time/ 100 mg of supported catalyst.

P- 80 °C/200 psig ethylene/ 30 min reaction time/ 100 mg of supported catalyst.

Gas Phase Polymerization (Part 1)

Ex.	Catalyst	Procedure	Mass Polymer (g)	Total TO	M_n	PDI	Branches/ 1000C (^{1}HNMR)	T_m (° C)
120	A	A	11.5	395K	164K	3.21	8	128
121	A	B	8.5	293K	174K	3.59	9	124
122	A	C	6.5	224K	124K	4.14	14	120
123	A	D	4.7	160K	126K	4.01	21	117
124	A	E	3.5	121K	91K	3.67	28	119
125	A	F	4.3	110K	94K	3.33	27	118
126	A	G	9.8	336K	121K	3.51	13	121
127	H	B	13.5	231K	133K	3.22	10	122
128	H	G	12	206K	117K	3.39	13	121
129	H	E	9.4	161K	106K	3.57	26	115
130	H	H	7.8	267K	195K	3.16	9	123
131	B	E	14	48K	60K	4.42	48	114
132	B	I	3	41K	94K	3.2	36	114
133	B	J	6.8	47K	88K	3.49	36	119
134	C	J	9	61K	89K	3.94	34	119
135	B	K	4.4	30K	48K	4.14	53	113
136	C	K	5.6	38K	63K	3.63	45	116
137	B	L	8	55K	93K	3.57	28	118
138	C	L	12	82K	91K	3.79	30	119

isolated by dissolving the NaCl in a blender and collecting the remaining polymer by filtration. The polyethylene was washed with 6M HCl, water and actetone. The polymer was then dried in a vacuum oven at 100 °C.

A- 80 °C/800 psig ethylene/ 20 min reaction time/ 200 mg of supported catalyst.

B- 65 °C/400 psig ethylene/ 60 min reaction time/ 200 mg of supported catalyst.

C- 65 °C/200 psig ethylene/ 60 min reaction time/ 200 mg of supported catalyst.

D- 65 °C/100 psig ethylene/ 60 min reaction time/ 200 mg of supported catalyst.

E- 80 °C/100 psig ethylene/ 60 min reaction time/ 200 mg of supported catalyst.

F- 80 °C/200 psig ethylene/ 60 min reaction time/ 200 mg of supported catalyst.

G- 80 °C/400 psig ethylene/ 60 min reaction time/ 200 mg of supported catalyst.

H- 80 °C/400 psig ethylene/ 60 min reaction time/ 100 mg of supported catalyst.

I- 80 °C/100 psig ethylene/ 60 min reaction time/ 50 mg of supported catalyst.

J- 80 °C/100 psig ethylene/ 60 min reaction time/ 100 mg of supported catalyst.

K- 100 °C/100 psig ethylene/ 60 min reaction time/ 100 mg of supported catalyst.

L- 80 °C/200 psig ethylene/ 60 min reaction time/ 100 mg of supported catalyst.

M- 100 °C/200 psig ethylene/ 60 min reaction time/ 100 mg of supported catalyst.

C- **XXVII**/MAO on Silica (Witco)/0.3 mg of **XXVII** per gram silica/extra MAO added. See example 118 as a representative example.

D- **XXVII**/ Silica (Grace Davison XPO-2402)/MAO solution/1.5 mg of **XXVII** per gram silica. See example 117 as a representative example.

E- **XXVII**/MAO on Silica (Witco)/0.6 mg of **XXVII** per gram silica/extra MAO added. See example 118 as a representative example.

F- **XXVII**/MAO on Silica (Witco)/0.6 mg of **XXVII** per gram silica/extra TMA added. See example 116 as a representative example.

G- **XXVII**/ Silica (Grace Davison XPO-2402)/TMA solution/0.6 mg of **XXVII** per gram silica. See example 117 as a representative example.

H- **XXVII**/MAO on Silica (Witco)/0.6 mg of **XXVII** per gram silica. See example 115 as a representative example.

Gas Phase Polymerization Procedure

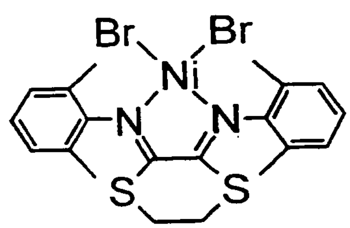
The basic procedure involves loading a 600 ml Parr® stirred autoclave with 300 g of NaCl (dried in a vacuum oven at 100 °C for 24 hours) and a known amount of supported **XXVII** catalyst. The ethylene homopolymerization reactions summarized below were run between 50 °C and 80 °C and 100 and 1000 psig ethylene. The resulting polyethylene was

Example 119

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 6 mg (10 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of silica (Grace Davison XPO-2402). The solid mixture was cooled to 0 °C in an ice bath and 20 ml of hexane and 2 ml of a TMA solution in toluene was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour, the solvent was removed *in vacuo* giving 0.94 g of supported catalyst.

Gas Phase Polymerization



XXVII

Catalysts Preparation

A- **XXVII**/MAO on Silica (Witco)/0.3 mg of **XXVII** per gram silica. See example 115 as a representative example.

B- **XXVII**/MAO on Silica (Witco)/3 mg of **XXVII** per gram silica. See example 92 as a representative example.

addition of 2 ml (4 mmol) of trimethylaluminum (TMA). The mixture was stirred at 0 °C for one hour. The solvent was removed in *vacuo* along with excess TMA leaving the supported catalyst system.

Example 117

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 15 mg (26 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of silica (Grace Davison XPO-2402). The solid mixture was cooled to 0 °C in an ice bath and 20 ml of toluene and 7 ml of a MAO solution in toluene was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour, the solvent was removed *in vacuo* giving 1.3 g of supported catalyst.

Example 118

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 18 mg (31 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 3 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 25 ml of CH_2Cl_2 was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour, the solvent was removed *in vacuo* giving a brown supported catalyst material. The supported catalysts was then suspended in 20 ml of hexane followed by addition of 0.5 ml of MAO. The mixture was stirred at 0 °C for one hour. The solvent was removed in *vacuo* leaving 2.9 g of the supported catalyst.

several hours in a vacuum oven at 100 °C resulting in 1.4 g of a white powdery solid (2700 TO/h based on 100 % active catalyst). ^{1}H NMR indicates 1 wt % ethyl undecenoate incorporated into the copolymer.

Obviously, numerous modifications and variations of the present invention are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended Claims, the invention may be practiced otherwise than as specifically described herein.

Example 115

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 9 mg (16 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 3 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 25 ml of toluene was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour, the solvent was removed *in vacuo* giving 2.8 g of supported catalyst material.

Example 116

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]-dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 6 mg (10 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 20 ml of CH_2Cl_2 was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour, the solvent was removed *in vacuo* giving a brown supported catalyst material. The supported catalysts was then suspended in 20 ml of hexane followed by

atoms. DSC: (2nd heat) melt endothermic maximum at 118 °C. GPC: M_n = 150,000; M_w/M_n = 3.10.

Example 113

Copolymerization of ethylene and ethyl undecenoate using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared as described in example 92.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 100 mg of the nickel /MAO treated silica supported catalyst system. The flask was placed under an ethylene atmosphere, and 45 mL of toluene and 2.5 mL of ethyl undecenoate was added, giving a purple suspension. The polymerization was left to stir for 5 hours at 0 °C. After 5 hours at 0 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The white copolymer was isolated by filtration, washed with copious amounts of acetone and dried for several hours in a vacuum oven at 100 °C resulting in 1.3 g of a white powdery solid (1800 TO/h based on 100 % active catalyst). ^{1}H NMR indicates 1 wt % of ethyl undecenoate incorporated into the copolymer.

Example 114

Copolymerization of ethylene and ethyl undecenoate using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared as described in example 92.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 100 mg of the nickel /MAO treated silica supported catalyst system. The flask was placed under an ethylene atmosphere, 45 mL of toluene and 2.5 mL of ethyl undecenoate was added giving a purple suspension. The polymerization was left to stir for 3.5 hours at 23 °C. After 3.5 hours at 23 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The white copolymer was isolated by filtration, washed with copious amounts of acetone and dried for

acetone and 6 N HCl. The polymer which separated was isolated by filtration and dried *in vacuo* to afford 0.177 g of white, powdery polyethylene. DSC: (2nd heat) melt endothermic maxima at ca. 100, 106 and 127 °C. GPC: M_n = 1,100 g/mol; M_w/M_n = 15.5.

Example 111

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2-*tert*-butylphenylimino)-[1,4]dithiane.

A 500 mL flame-dried pear-shaped flask equipped with a magnetic stir bar and capped by a septum was charged with 100 mg of the supported nickel complex of 2,3-bis(2-*tert*-butylphenylimino)-[1,4]dithiane prepared in Example 108. The flask was evacuated and refilled with ethylene, then treated with 50 mL of dry, deoxygenated toluene and stirred under 1 atm ethylene at 23 ^{0}C for 125 min. The reaction was quenched by the addition of methanol, acetone and 6 N HCl. The polymer which separated was isolated by filtration and dried *in vacuo* to afford 0.529 g of white, powdery polyethylene. DSC: (2nd heat) melt endothermic maxima at 96 and 110 °C. ^{1}H NMR (o-dichlorobenzene): 36 branches/1000 carbon atoms. GPC: M_n = 120,000; M_w/M_n = 2.46.

Example 112

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 500 mL flame-dried pear-shaped flask equipped with a magnetic stir bar and capped by a septum was charged with 106 mg of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane prepared in Example 109. The flask was evacuated and refilled with ethylene, then treated with 50 mL of dry, deoxygenated toluene and stirred under 1 atm ethylene at 23 ^{0}C for 255 min. The reaction was quenched by the addition of methanol, acetone and 6 N HCl. The polymer which separated was isolated by filtration and dried *in vacuo* to afford 3.2 g of white, powdery polyethylene. ^{1}H NMR (o-dichlorobenzene): 20 branches/1000 carbon

nickel dibromide complex of 2,3-bis(2-*tert*-butylphenylimino)-[1,4]dithiane and 1.0 g of MAO treated silica (Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 25 mL of dry, deoxygenated CH_2Cl_2 was added. The reaction was stirred at 0 °C for 50 min, then the volatiles were removed by evaporation under reduced pressure (0.2 torr) at 0 °C for 40 min to afford the supported catalyst as a light brown powder which was stored under nitrogen at –25 °C.

Example 109

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane.

A 500 mL flame-dried pear-shaped flask equipped with a magnetic stir bar and capped by a septum was charged with 30 mg (55 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dioxane and 1.01 g of MAO treated silica (Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 25 mL of dry, deoxygenated CH_2Cl_2 was added. The reaction was stirred at 0 °C for 65 min, then the volatiles were removed by evaporation under reduced pressure (0.2 torr; 20 min at 0 °C, 75 min at 25 °C) to afford the supported catalyst as a brown powder which was stored under nitrogen at –25 °C.

Example 110

Polymerization of ethylene using the supported nickel complex of 2,3-bis(phenylimino)-[1,4]dithiane.

A 500 mL flame-dried pear-shaped flask equipped with a magnetic stir bar and capped by a septum was charged with 100 mg of the supported nickel complex of 2,3-bis(phenylimino)-[1,4]dithiane prepared in Example 107. The flask was evacuated and refilled with ethylene, then treated with 50 mL of dry, deoxygenated toluene and stirred under 1 atm ethylene at 23°C for 14 h. The reaction was quenched by the addition of methanol,

purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 96. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 30 °C. The reactor was rapidly pressurized to 100 psig ethylene. After 60 minutes at 30 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C resulting in 11.5 g of a white rubbery solid (160,000 TO/h). DSC: 2nd heat showed an endothermic maximum at 127 °C. GPC: Mn = 279,000; Mw/Mn = 2.73. ^{1}H NMR: 7 branches/1000 carbon atoms.

Example 107

Synthesis of the supported nickel complex of 2,3-bis(phenylimino)-[1,4]dithiane.

A 500 mL flame-dried pear-shaped flask equipped with a magnetic stir bar and capped by a septum was charged with 27 mg (52 µmol) of the nickel dibromide complex of 2,3-bis(phenylimino)-[1,4]dithiane and 1.0 g of MAO treated silica (Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 25 mL of dry, deoxygenated CH_2Cl_2 was added. The reaction was stirred at 0 °C for 50 min, then the volatiles were removed by evaporation under reduced pressure (0.2 torr) at 0 °C for 40 min to afford the supported catalyst as a light green-grey powder which was stored under nitrogen at –25 °C.

Example 108

Synthesis of the supported nickel complex of 2,3-bis(2-*tert*-butylphenylimino)-[1,4]dithiane.

A 500 mL flame-dried pear-shaped flask equipped with a magnetic stir bar and capped by a septum was charged with 34 mg (56 µmol) of the

removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 50 °C. The reactor was rapidly pressurized to 100 psig ethylene. After 60 minutes at 50 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C resulting in 6.5 g of a white rubbery solid (88,000 TO/h). DSC: 2nd heat showed a broad melt transition with an endothermic maximum at 119 °C. GPC: Mn = 182,600; Mw/Mn = 3.01. ^{1}H NMR: 19 branches/1000 carbon atoms.

Example 105

<u>Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 96.</u>

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 96. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 50 °C. The reactor was rapidly pressurized to 100 psig ethylene. After 60 minutes at 50 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C resulting in 5.4 g of a white rubbery solid (74,000 TO/h). DSC: 2nd heat showed abroad melt transition with an endothermic maximum at 120 °C. GPC: Mn = 186,500; Mw/Mn = 2.66. ^{1}H NMR: 18 branches/1000 carbon atoms.

Example 106

<u>Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 96.</u>

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then

resulting in 5.97 g of a white rubbery solid (41,000 TO/h). DSC: 2nd heat showed an endothermic maximum at 120 °C. GPC: Mn = 138,000; Mw/Mn = 2.95. ^{1}H NMR: 17 branches/1000 carbon atoms.

Example 103

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared according to the procedure described in example 92.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of supported catalyst. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 65 °C. The reactor was rapidly pressurized to 100 psig ethylene. After 60 minutes at 65 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C resulting in 9.0 g of a white rubbery solid (62,000 TO/h). DSC: 2nd heat showed an endothermic maximum at 116 °C. GPC: Mn = 83,500; Mw/Mn = 4.71. ^{1}H NMR: 35 branches/1000 carbon atoms.

Example 104

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 96.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 96. Upon

Example 101

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 93.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 93. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 50 °C. The reactor was rapidly pressurized to 90 psig ethylene. After 60 minutes at 50 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C resulting in 2.13 g of a white rubbery solid (30,000 TO/h). DSC: 2nd heat showed an endothermic maximum at 120 °C. ^{1}H NMR: 17 branches/1000 carbon atoms. GPC: Mn = 119,000; Mw/Mn = 2.93.

Example 102

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 94.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 94. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 50 °C. The reactor was rapidly pressurized to 90 psig ethylene. After 60 minutes at 50 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C

Example 99

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 92.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 92. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 100 °C. The reactor was rapidly pressurized to 90 psig ethylene and the temperature ramped up to 140 °C. After 60 minutes at 140 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100° C. GPC: Mn = 56,000; Mw/Mn = 7.19.

Example 100

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane prepared in example 95.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 100 mg of the supported catalyst prepared in example 95. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 50 °C. The reactor was rapidly pressurized to 90 psig ethylene. After 30 minutes at 50 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100° C resulting in 1.25 g of a white rubbery solid (18,000 TO/h). ^{1}H NMR: 62 branches/1000 carbon atoms. GPC: Mn = 336,000; Mw/Mn = 2.22.

Example 97

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 92.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 100 mg of the nickel /MAO treated silica supported catalyst system prepared in example 92. The flask was placed under an ethylene atmosphere and 50 mL of toluene was added giving a red/brown suspension. The polymerization was left to stir for 1 hour at 23 °C. After 60 minutes at 23 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100 °C resulting in 1.6 g of a white rubbery solid (11,000 TO/h based on 100 % active catalyst). DSC: (2nd heat) melt with an endothermic maximum at 118 °C. ^{1}H NMR: 30 branches/1000 carbon atoms. GPC: Mn = 208,000; Mw/Mn = 2.45.

Example 98

Polymerization of ethylene using the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane prepared in example 92.

A 600 mL Parr ® autoclave was first heated to about 100 °C under dynamic vacuum to ensure the reactor was dry. The reactor was then purged with argon. The 600 mL Parr ® autoclave was charged in the glove box with 200 mg of the supported catalyst prepared in example 92. Upon removing the autoclave from the box, 150 mL of toluene was added and the reactor was heated to 60 °C. The reactor was rapidly pressurized to 90 psig ethylene . After 60 minutes at 60 °C, the reaction was quenched by the addition of acetone, 6M HCl and methanol. The swollen polyethylene was isolated by filtration and dried for several hours in a vacuum oven at 100° C resulting in 22.5 g of a white rubbery solid (80,000 TO/h). ^{1}H NMR: 31 branches/1000 carbon atoms. GPC: Mn = 128,000; Mw/Mn = 2.58.

filter cannula and dried under dynamic vacuum giving 780 mg of supported catalyst.

Example 96

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 15 mg (26 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 20 mL of CH_2Cl_2 was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour the solvent was removed *in vacuo* resulting in 940 mg of a purple solid.

resulting purple silica support material was dried under dynamic vacuum giving 916 mg of supported catalyst material.

Example 94

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 30 mg (52 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 20 mL of toluene was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour the solid was allowed to settle and the solvent was removed via filter cannula. The resulting purple solid was washed with toluene using a filter cannula and was dried under dynamic vacuum giving 900 mg of supported catalyst material.

Example 95

Synthesis of the supported nickel complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 34 mg (50 μmol) of the nickel dibromide complex of 2,3-bis(2,6-diisopropylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 20 mL of CH_2Cl_2 was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour the solvent was removed *in vacuo*. The resulting red brown solid was washed with CH_2Cl_2 using a

hexene, and 2.0 mL of a 10 wt% solution of MAO in toluene, under Ar. The resultant clear yellow solution was stirred at 23 ^{0}C for 400 min, then the reaction was quenched with acetone, methanol and 6 N aq HCl, and the polyhexene which separated was filtered off and dried in vacuo (0.4 mm Hg) to obtain 408 mg of an elastic polyhexene. ^{1}H NMR: 90 branches/1000 carbon atoms. GPC: M_n = 47,000; M_w/M_n = 1.7.

Example 92

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 30 mg (52 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 25 mL of the CH_2Cl_2 was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour the solvent was removed *in vacuo*. The resulting purple solid was washed with CH_2Cl_2 using a filter cannula and dried under dynamic vacuum.

Example 93

Synthesis of the supported nickel complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane.

A flame dried pear-shaped flask equipped with a stir bar and a septum was charged with 15 mg (26 μmol) of the nickel dibromide complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane and 1 g of MAO treated silica (purchased from Witco TA 02794/HL/04). The solid mixture was cooled to 0 °C in an ice bath and 20 mL of toluene was added. The reaction was rapidly stirred at 0 °C for 1 hour. After 1 hour the solid was allowed to settle and the solvent was removed via filter cannula. The resulting purple solid was washed with toluene using a filter cannula. The

complex of 2,3-bis(2,6-dimethylphenylimino)-[1,4]dithiane, 4.0 mL 1-hexene, and 2.0 mL of a 10 wt% solution of MAO in toluene, under Ar. The resultant violet mixture thickened noticably within minutes. After 34 min, the reaction was quenched with acetone, methanol and 6 N aq HCl, and the polyhexene which separated was filtered off and dried in vacuo (0.4 mm Hg) to obtain 428 mg of an elastic polyhexene. ^{1}H NMR: 173 branches/1000 carbon atoms. GPC: M_n = 92,000; M_w/M_n = 2.0.

Example 90

Polymerization of 1-hexene with the nickel dibromide complex 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole in the presence of MAO.

A 22 mL vial equipped with a magnetic stir bar and capped by a septum was sequentially charged with 2.1 mg of the nickel dibromide complex 2,3-bis(2,6-dimethylphenylimino)-2,3-dihydroimidazo[2,1-*b*]thiazole, 4.0 mL 1-hexene, and 2.0 mL of a 10 wt% solution of MAO in toluene, under Ar. The resultant dark purple-brown mixture thickened noticably within 10-20 minutes. After 53 min, the reaction was quenched with acetone, methanol and 6 N aq HCl, and the polyhexene which separated was filtered off and dried in vacuo (0.4 mm Hg) to obtain 283 mg of an elastic polyhexene. ^{1}H NMR: 110 branches/1000 carbon atoms. GPC: M_n = 91,000; M_w/M_n = 1.9.

Example 91

Polymerization of 1-hexene with the nickel dibromide complex of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine in the presence of MAO.

A 22 mL vial equipped with a magnetic stir bar and capped by a septum was sequentially charged with 2.1 mg of nickel dibromide complex of 1,4-dimethyl-2,3-bis(2,6-dimethylphenylimino)piperazine, 4.0 mL 1-